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RAMAN SPECTRA OF THE HYDROCARBON CYPERENE II

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(Communicated by Professor R. S. Krishnan, F.A.SC.)

1. Introduction

From the tubers of the weed plant *Cuperus rotundus* L., Kimura and Ohtani (1928) obtained an oil which on fractional distillation gave three main products, hydrocarbon, alcoholic and ketonic and these were named cyperene, cyperol and cyperone respectively. Hegde and Rao (1935) have examined the oil of *Cyperus rotundus* tubers of Indian variety but they could not detect the hydrocarbon of properties mentioned by Kimura and Ohtani and they suggested that there were at least two different hydrocarbons present.

A more thorough investigation of the hydrocarbon fraction of the oil from Indian tubers (Madras variety) was undertaken by one of us (Senich) and it was found that by fractional distillation, four hydrocarbon fractions could be separated two of them in very small amounts and two with 6% and 14% yield. The product with 14% yield which we call cyperene II was subjected to partial hydrogenation [with $Pd(OH)_2$ as catalyst] equivalent to removing one double bond. The compound still showed unsaturation (test with tetranitromethane). On hydrogenation with PtO_2 as catalyst and acetic acid as solvent it was found that the compound was completely saturated after absorption of hydrogen equivalent to two double bonds.

It is considered that an investigation of the Raman spectra of cyperene II along with its partially hydrogenated and fully hydrogenated products may help in determining the nature and position of the double bonds. The results of such an investigation are presented in this paper.

2. Experimental Details

The Raman spectra of the three hydrocarbons (Cyperene II, Dihydrocyperene II and Tetrahydrocyperene II) were obtained in the liquid state

with a Hilger two prisms spectrograph having a dispersion of 27 A/mm. in the λ 4358 region. The liquids freshly distilled over sodium were taken in a small pyrex tube having a flat plate fused at one end. This was inserted into a similar tube of larger diameter and the space between the tubes was filled with a fairly saturated solution of sodium nitrite in water to serve as filter. Two vertical pyrex arcs were used as light source and the scattered light was reflected by means of a right angle prism and then focussed on the slit of the spectrograph with a condensing lens. An iron arc comparison spectrum was also taken side by side on each plate.

3. Results and Discussions

The Raman shifts of the three samples are given in Table I along with visually estimated intensities. The microphotometer records in the region 1000–17000 cm.$^{-1}$ and the enlarged reproductions of the spectra are given in Plates XI and XII.

TABLE I

Frequency Shifts in Wave Numbers

Cyperene II	Dihydrocyperene II	Tetrahydrocyperene II
142 (6)	144 (2)	259 (1 *b*)
269 (4 *b*)	263 (2 *b*)	
295 (4 *b*)	295 (2 *b*)	
346 (2 *b*)	346 (2)	
434 (1)	440 (1 *b*)	
608 (3)	608 (2)	613 (2)
	668 (1)	
695 (3)	707 (2)	703 (3)
732 (2)		
796 (2)	796 (2)	
	848 (2)	
879 (5)	879 (0)	
947 (2)	949 (2)	949 (1 *b*)
993 (2)	993 (2)	993 (1 *b*)
1365 (2 *b*)	1379 (2 *b*)	1379 (2 *b*)
1448 (8 *b*)	1450 (8 *b*)	1450 (6 *b*)
1599 (3)		
1645 (10)		
	1665 (5)	
2852 (5 *b*)	2858 (6 *b*)	2852 (6 *b*)
2920 (8 *b*)	2920 (8 *b*)	2925 (8 *b*)
2966 (5)	2963 (8 *b*)	2965 (8 *b*)
3041 (2)	3048 (2)	
3076 (2)		

The Raman spectrum of cyperene II (compound I) shows a strong line at 1645 cm.$^{-1}$ and a weak line at 1599 cm.$^{-1}$ In dihydrocyperene II (compound II) there is one line at 1665 cm.$^{-1}$ of medium intensity whereas in tetrahydrocyperene II (compound III) there is no line in that region between 1500 and 1700 cm.$^{-1}$ These may be taken as evidence for the presence of two double bonds (C = C) in compound I, one double bond in compound II, and no double bond at all in compound III. In compound I the line at 1645 cm.$^{-1}$ is found to be more intense than the line at 1450 cm.$^{-1}$, whereas the line at 1665 cm.$^{-1}$ of compound II is only half as intense as the line at 1450 cm.$^{-1}$ If one of the double bonds of compound I is to be identical with the double bond of compound II the frequency shifts corresponding to these will also be expected to be the same. But actually it is observed that in compound I the shift is about 20 cm.$^{-1}$ less than that in compound II but of much greater intensity. This enhanced intensity and lowering of frequency can be explained if it is assumed that there exists conjugation between the double bonds. The line at 1665 cm.$^{-1}$ probably corresponds to the value of a trisubstituted ethylenic linkage. This is slightly lower than the normal value (1675 cm.$^{-1}$) of a trisubstituted C = C linkage. An alternative explanation of this can be given on the basis of the existence of an $R_1R_2C = CH_2$ group in the dihydrogenated compound also.

In compound I there exists a strong line at 879 cm.$^{-1}$ and a line of medium intensity at 796 cm.$^{-1}$ which can be assigned respectively to the hydrogen out of plane deformation in the asymmetric disubstituted ethylenic group $R_1R_2C = CH_2$ and of the trisubstituted group $R_1R_2C = CHR_3$. The intensity of the line 879 cm.$^{-1}$ is found to be more than twice as much as the line at 796 cm.$^{-1}$ In compound II the line 879 cm.$^{-1}$ is considerably reduced in intensity compared to 796 cm.$^{-1}$ indicating probably the removal or the reduction in the number of the group $R_1R_2C = CH_2$ in that compound.

Another evidence for the occurrence of the two groups mentioned above in compound I is the appearance of the lines 3076 and 3041 cm.$^{-1}$ In compound II only the second line is present but in compound III both are absent. These lines are to be ascribed (Bellamy, 1954) to the C–H stretching vibrations in the groups $R_1R_2C = CH_2$ and $R_1R_2C=CHR_3$ respectively. However since the lines are of very week intensity it is not possible to draw definite conclusions about the presence of these groups.

Detailed chemical investigations carried out by Senich and Sukh Dev (1955) on the structure of cyperene II indicated the presence of two double bonds and certain possible positions for these have been postulated. The results on the Raman spectra presented above enables us to suggest that

the molecule of cyperene II contains two double bonds, one of the asymmetric disubstituted type while the other one may also be of the same type or in such a position as to favour conjugation.

SUMMARY

The Raman spectra of cyperene II isolated from the hydrocarbon fraction of the oil from weed plant has been studied along with its partially hydrogenated product, dihydrocyperene II and fully hydrogenated product tetrahydrocyperene II. The spectra indicate the presence of two double bonds in cyperene II, one double bond in dihydrocyperene II and no double bond at all in tetrahydrocyperene II. The nature of these double bonds in relation to the observed spectra has been discussed.

In conclusion the authors wish to express their grateful thanks to Professor R. S. Krishnan, Head of the Department of Physics, and Professor K. Banerjee, Head of the Department of Organic Chemistry, and to Dr. Sukh Dev of the Department of Organic Chemistry, for helpful discussions.

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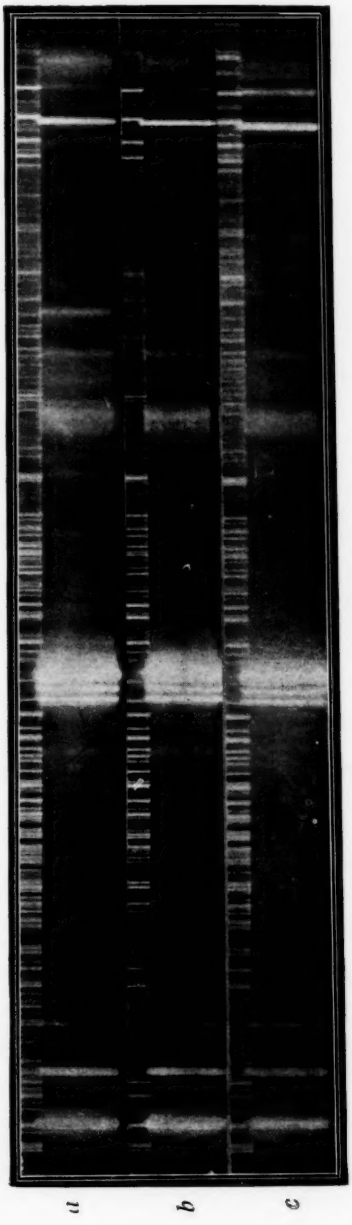

FIG. 1

(*a*) Raman spectrum of cyperene II
(*b*) " of dihydrocyperene II
(*c*) " of tetrahydrocyperene II

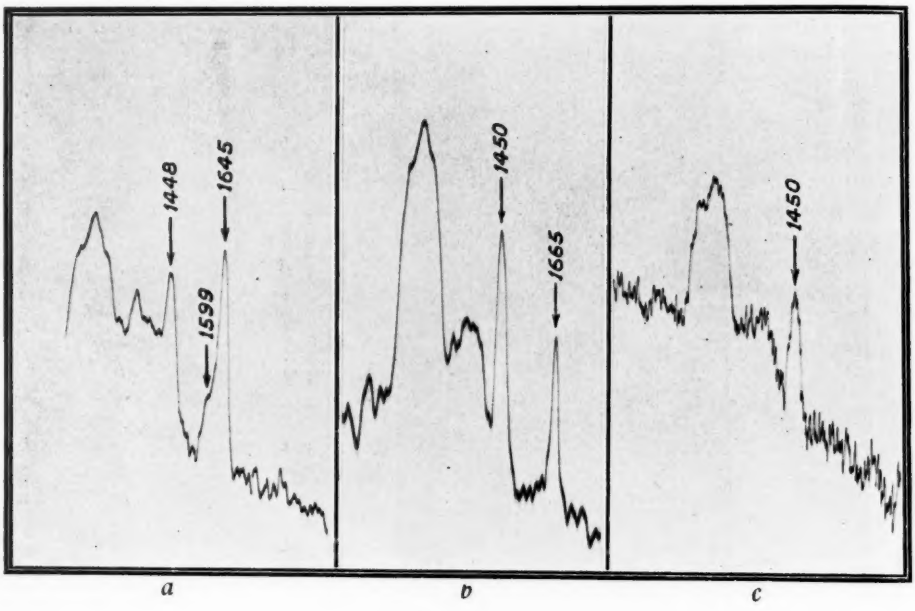

FIG. 2

Microphotometer records in the region 1,000 to 1,700 cm.
(*a*) Cyperene II; (*b*) Dihydrocyperene II; (*c*) Tetrahydrocyperene

HETEROCYCLIC COMPOUNDS

Part VI*. Synthesis of Substituted Pyrido-(1, 2 *a*)-pyrimidine-2-ones

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Received November 19, 1955

(Communicated by Dr. K. N. Menon, F.A.SC.)

THE synthesis of 3, 4-dihydro-2 H-pyrido-(1, 2 *a*)-pyrimidine-2-one has been reported by a number of workers. Adams and Pachter,[1] and Kirpal and Wojnar[2] reacted 2-amino-pyridine with β-halageno-propionic acid or the ester using ethanol or chloroform as the medium. Magidson and Elina[3] obtained the hydrochlorides of 3, 4-dihydro-2 H-pyrido-(1, 2 *a*)-pyrimidine-2-one by the hydrolysis of the reaction product of sulphapyridine and ethyl 3-bromo-propionate with hot concentrated hydrochloric acid. In a second synthesis by the same authors, 2-amino-pyridine and ethyl 3-bromo-propionate were refluxed in boiling ethanol. Hurd and Shin Hayao[4] condensed 2-amino-pyridine with propiolactone to yield the pyrimidone.

As part of a scheme of study of heterocyclic systems in progress in this laboratory, the syntheses of methyl substituted pyrido-(1, 2 *a*)-pyrimidine-2-ones were undertaken. Methyl-2-amino-pyridine, with the exception of the 6-methyl derivative, reacted homogeneously with β-iodo-propionic acid to afford the desired 3, 4-dihydro-2 H-pyrido-(1, 2 *a*)-pyrimidine-2-ones as hydriodides. In the case of the 6-methyl-2-amino-pyridine two products were obtained. The desired pyrimidine-2-one was obtained only in a low yield, about 30% only. This is in agreement with other reports. Lappin[5] has shown that 2-amino-pyridine carrying a methyl or any electron releasing substituent in position-6, reacts with ethoxy methylene malonic ester to give the 1, 8-naphthyridine derivative rather than the expected pyrido-(1, 2 *a*)-pyrimidone. This is attributed to the stearic hindrance of the 6-methyl group. The second compound obtained in the present work from 6-methyl-2-amino-pyridine is under further scrutiny.

EXPERIMENTAL

9-Methyl-3, 4-dihydro-2 H-pyrido-(1, 2 a)-pyrimidine-2-one

A solution of 4·3 g. (0·04 mole) of 3-methyl-2-amino-pyridine and 8·0 g. (0·04 mole) of β-iodo-propionic acid in 30 ml. of chloroform was refluxed

* Part V: *J. Madras University*, 1955, **25 B**, 125.

on a water-bath for 24 hours with occasional shaking. After cooling, the solid product was collected, dissolved in absolute methanol and precipitated with ether to give 7·2 g. (62%) of the hydriodide, m.p. 243-45°. Two crystallisations from methanol-ether mixture raised the melting point to 247–248·5°. The same product was obtained in an identical yield by reacting the two components in the absence of any solvent (Found: C, 37·9; H, 4·2; N, 9·7. Calculated for $C_9H_{10}N_2O.HI$: C, 37·2; H, 3·8; N, 9·7.)

The picrate was obtained by mixing the alcoholic solutions of the hydriodide and picric acid. It crystallised in yellow platelets from methanol, m.p. 166–67°. (Found: N, 17·3. Calculated for $C_9H_{10}N_2O.C_6H_3N_3O_7$; N, 17·9.)

Isolation of the base

The hydriodide (5 g.) was added with stirring to 35 ml. of a saturated aqueous potassium carbonate solution, extracted with chloroform, and the extract dried over anhydrous potassium carbonate. On concentrating the chloroform solution and storing in a refrigerator, the product crystallised. It separated from methanol in white platelets, m.p. 221°. (Found: N, 16·8. Calculated for $C_9H_{10}N_2O$: N, 17·3.)

8-*Methyl*-3, 4-*dihydro*-2 *H-pyrido*-(1, 2 a)-*pyrimidine*-2-*one*

Condensation of 2·16 g. (0·02 mole) of 4-methyl-2-amino-pyridine with 4 g. (0·02 mole) of β-iodopropionic acid yielded 3·5 g. (60%) of the pyrimidone, m.p. 236–38° (from methanol). (Found: C, 38·0; H, 4·2; N, 9·8. Calculated for $C_9H_{10}N_2O.HI$: C, 37·2; H, 3·8; N, 9·7.)

The picrate crystallised from water in yellow plates, m.p. 169–70°. (Found: C, 46·8; H, 3·2. Calculated for $C_9H_{10}N_2O.C_6H_3N_3O_7$; C, 46·1; H, 3·3.)

The base liberated from the salt was too hygroscopic to permit purification.

7-*Methyl*-3, 4-*dihydro*-2 *H-pyrido*-(1, 2 a)-*pyrimidine*-2-*one*

2·2 g. of 5-methyl-2-amino-pyridine, on condensation with 4 g. of β-iodopropionic acid, afforded 3·2 g. of the pyrimidone of m.p. 275–78° (decomp.) (from absolute methanol). (Found: C, 37·7; H, 4·0; N, 10·2. Calculated for $C_9H_{10}N_2O{\cdot}HI$; C, 37·2; H, 3·8; N, 9·7.)

The picrate crystallised from water, m.p. 170–71°. (Found: C, 46·6; H, 3·0. Calculated for $C_5H_{10}N_2O.C_6H_3N_3O_7$; C, 46·1; H, 3·3.)

The free base, although it melted somewhat sharply at 183–85°, was too hygroscopic to be obtained in analytical purity.

6-Methyl-3, 4-dihydro-2 H-pyrido-(1, 2 a)-pyrimidine-2-one

6-Methyl 2-amino-pyridine yielded two products on condensation with β-iodo-propionic acid. One product was obtained in 30% yield on fractional crystallisation of the crude condensation product from methanol. On repeated crystallisation from methanol, it was obtained in white prisms, m.p. 260–63°° (decomp.). (Found: C, 37·2; H, 3·4; N, 10·0. Calculated for $C_9H_{10}N_2O.HI$: C, 37·2; H, 3·8; N, 9·7.)

The free base liberated from the above was too hygroscopic to work with. The picrate could not be purified.

The second product, crystallised from methanol-ether mixture in white needles, m.p. 152°.

3, 4-Dihydro-2 H-pyrido-(1, 2 a)-pyrimidine-2-one

2-Amino-pyridine (1·9 g.) and β-iodo-propionic acid (4·6 g.) dissolved in 30 ml. of chloroform, were refluxed on the water-bath for 6 hours. The product crystallised from methanol in white platelets. m.p., 263–64°. (Found: N, 10·2. Calculated for $C_8H_8N_2O.HI$: N, 10·6.)

The free base melted at 188–90° corresponding to that recorded by Adams and Pachter.[1]

I take this opportunity to express my thanks to Dr. K. N. Menon for guidance during the course of this work and the University of Madras for the award of a scholarship. I wish to thank Mr. S. Selvanayagam for carrying out the micro-analyses.

Summary

The synthesis of a number of pyrido-(1, 2 *a*)-pyrimidine-2-ones is reported. All of them exhibited a violet fluorescence in chloroform.

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PARAMAGNETIC RESONANCE IN SOME CUPRIC SALTS

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Received November 18, 1955

(Communicated by Professor R. S. Krishnan, F.A.SC.)

Introduction

The magnetic field dependent absorption of very high frequency waves by paramagnetic substances was discovered by Zavoisky (1945). Following the discovery of ' Paramagnetic Resonance ', Cummerow and Halliday (1946) investigated the same phenomenon using modern microwave techniques. Bagguley and Griffiths (1947) took up the case of chrome alum.

Cupric salts have interesting magnetic properties and a study of the paramagnetic resonance spectra in these offer an idea of the nature of the magnetic and electric interactions in crystals. When the orbital momentum is quenched due to internal electric fields and the spin $S=\frac{1}{2}$, the spectroscopic splitting factor 'g' is given by,

$$g_{\parallel}= 2-(4 \pm 4)\,\lambda/\Delta,$$

$$g_{\perp}= 2-(4 \mp 2)\,\lambda/\Delta$$

where λ is the spin-orbit coupling and is of the order of -852 cm.$^{-1}$ and Δ is the splitting between the orbital doublet and triplet states produced by the crystalline field. The signs $\pm$ should be chosen according as the doublet or triplet is lower respectively.

Experimental Set-up

Power is fed from a klystron microwave energy generator to a cavity resonator through a rectangular wave-guide and the output from the resonator is rectified by a crystal detector. The rectified current is read by means of a sensitive galvanometer. The frequency of the microwaves is measured by means of a cavity absorption wavemeter. The specimen under investigation is kept on either end of the cavity resonator where the microwave magnetic field is maximum, the dielectric absorption minimum and its direction parallel to the axis of the cavity resonator. A magnetic field is applied perpendicular to this microwave magnetic field. When the intensity of the externally applied magnetic field is equal to the resonance value, absorption

of the microwave energy by the paramagnetic salt takes place and there is a dip in the galvanometer deflection. The quantum of the microwave energy $h\nu$ and the resonant value of the magnetic field H_{res} are connected by the relation

$$h\nu = g\beta H_{res}$$

where β is the Bohr magneton and 'g' the spectroscopic splitting factor.

The magnetic field is calibrated by means of proton magnetic resonance and checked by the paramagnetic resonance of manganous salts whose spectroscopic splitting factor is accurately known.

Preparation of Compounds

Cupric Oxalate.—This is prepared by the action of oxalic acid on cupric cholride, when a bluish white precipitate is obtained. The precipitate was used for measurements after being washed several times with distilled water and dried well.

Cupric-Sodium-Oxalate.—When an oxalate is added to a cupric salt, a precipitate of cupric-oxalate is obtained at first. If an excess of the salt is added, the precipitate dissolves to a blue solution.

An excess of sodium oxalate (filtered) solution is added to a solution of cupric chloride and the blue solution of cupric-sodium-oxalate thus formed after removing the traces of sodium chloride which easily dissolves in water, is kept for crystallisation. The crystals are long and needle-shaped.

Cupric-Potassium-Oxalate.—Similarly a blue solution of cupric-potassium-oxalate is obtained by adding an excess of potassium-oxalate to cupric chloride solution. Here too only needle-like crystals like those of cupric-sodium-oxalate are obtained at first. If these crystals are allowed in solution for a longer time they crystallise as triclinic pinacoidal crystals which are dihydrate and isomorphous with cupric-ammonium-oxalate.

Cupric-Ammonium-Oxalate.—Crystals obtained by evaporating the blue solution of an excess of ammonium oxalate on cupric chloride at room temperature are also triclinic pinacoidal. They grow in the form of somewhat elongated hexagonal tablets, the slightly longer axis being parallel to the *a*-axis (Groth *b*-axis).

Cupric-Formate-Tetrahydrate.—Crystals of cupric-formate-tetrahydrate are prepared by the action of formic acid on cupric oxide and crystallised in the presence of formic acid to form monoclinic crystals.

Cupric-Butyrate-Monohydrate.—Cupric-butyrate-monohydrate prepared by the action of butyric acid on cupric-oxide gives deep green six-sided thick

crystals when an acetone solution of this is allowed to evaporate at room temperature.

RESULTS AND DISCUSSION

Powder Data.—Paramagnetic resonance curves of cupric-oxalate, cupric-sodium-oxalate and cupric-potassium-oxalate in powder form are shown in Fig. 1.

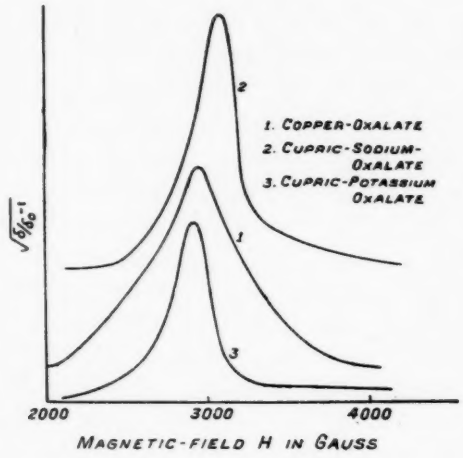

FIG. 1. Paramagnetic Resonance Curves of the Powders.

The 'g' values and the line widths* of the powders are given in Table I. The frequency at which these measurements were taken is in the 8820-8970 Mc. range.

TABLE I

Substance	'g' value	Line-width ($\Delta H_{\frac{1}{2}}$) gauss.
Cupric-Oxalate	2·12	720
Cupric-Sodium-Oxalate	2·07	325
Cupric-Potassium-Oxalate 2 H_2O ..	2·13	270
Cupric-Ammonium-Oxalate 2 H_2O ..	2·1	200

* The line-width is taken as *the width of* the resonance line *at half-power.*

The 'g' value and $\Delta H_{\frac{1}{2}}$ of cupric-oxalate powder as reported by Lancaster and Gordy (1951) are 2·07 and 120 gauss respectively.

CUPRIC-AMMONIUM-OXALATE DIHYDRATE. $Cu(NH_4)_2(C_2O_4)_2\,2\,H_2O$

This belongs to the triclinic centro-symmetrical class. These crystals grow in the form of hexagonal tablets, the longer dimension being the *b*-axis according to Groth. Sometimes they grow in the form of parallelopipeds.

According to preliminary investigations of X-ray analysis done in this laboratory, the cell dimensions are given by

$a = 8{\cdot}91$ Å*u* (Groth *b*-axis)

$b = 10{\cdot}65$ Å*u*

$c = 6{\cdot}94$ Å*u*

$\alpha = 122° 35'$; $\beta = 83° 52'$; $\gamma = 109° 7'$; Density = 1·94 gm./c.c. at room temperature thus giving two molecules per unit cell as in other similar copper salts.

The paramagnetic resonance curve of cupric-ammonium-oxalate in powdered form is shown in Fig. 2, the 'g' value being 2·1 and the line-width 200 gauss as given in Table I.

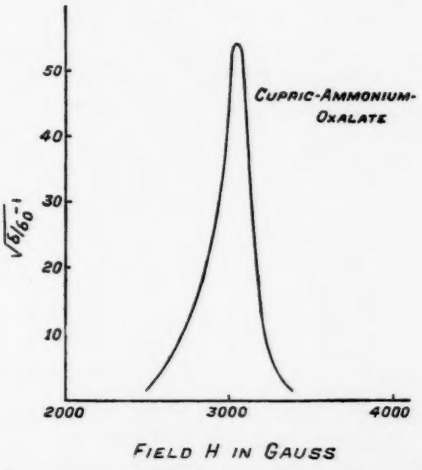

FIG. 2. Paramagnetic Resonance Curve of Cupric-Ammonium-Oxalate in Powder Form.

The anisotropy of 'g' values and line-widths has been studied in the (100), (010) and (001) planes of a single crystal. In each case the crystal is mounted on the upper choke plunger of the resonator to which is attached

a graduated rotating disc and magnetic measurements are taken at intervals of 10° each.

The polar diagrams showing the anisotropy of line-widths and curves showing the variation of 'g' value with orientation in different planes are shown in Figs. 3 to 7.

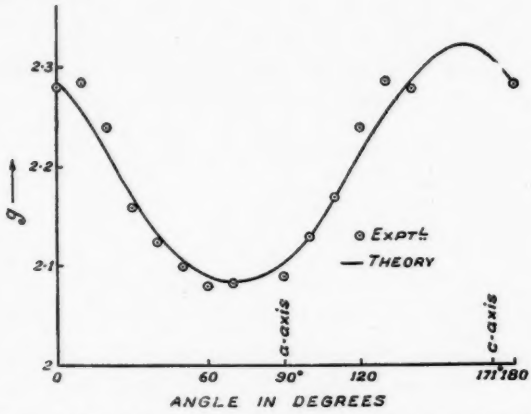

FIG. 3. Anisotropy of 'g' value in the (010) plane of Cupric-Ammonium-Oxalate Crystal.

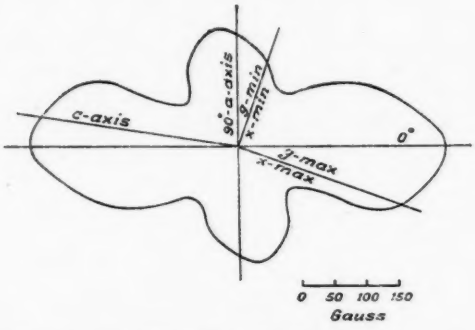

FIG. 4. Anisotropy of line-width in the (010) plane of Cupric-Ammonium-Oxalate Crystal.

The polar diagram (Fig. 4) showing the anisotropy of line-widths in the (010) plane consists of two pairs of lobes, the maxima lying practically along the directions of the crystallographic axes. On the basis of pure dipolar broadening one expects the maximum number of Cu^{++} ions in those directions. To a first approximation, the exchange interaction is taken to be isotropic and the influence of this is to produce an over-all shrinkage of the curve.

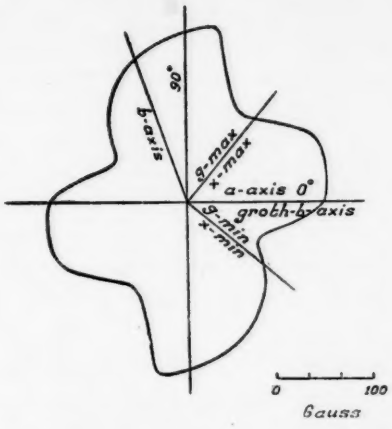

FIG. 5. Anisotropy of line-width in the (001) plane of Cupric-Ammonium-Oxalate.

In the (001) plane also (Fig. 5) the shape of the curve is almost similar to the previous one, showing maximum line-widths along the crystallographic axes, the line-widths being smaller owing to the longer dimensions of the cell edges.

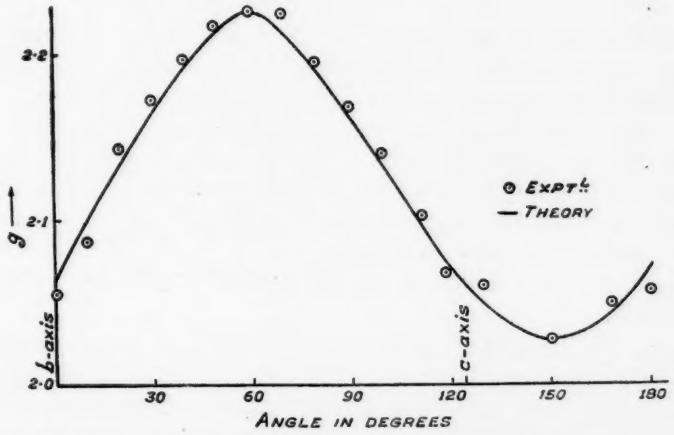

FIG. 6. Anisotropy of '*g*' value in the (100) plane of Cupric-Ammonium-Oxalate.

In the (100) plane (Fig. 7), the polar diagram is quite different from the other two in that the maximum line-width lies in a direction making an angle of about 50° with the *b*-axis, *i.e.*, approximately along the shorter diagonal of the (100) face in the unit cell. Hence we may expect the largest number

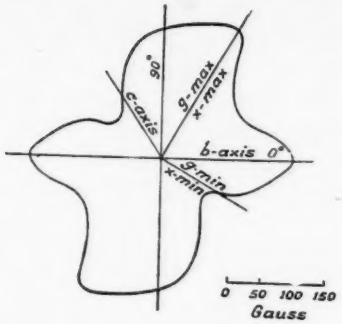

FIG. 7. Anisotropy of line-width in the (100) plane of Cupric-Ammonium-Oxalate.

of Cu^{++} ions along the shorter diagonal of the (100) face. Also the smallest line-widths are found in this plane and the minimum is in a direction making an angle of 140° with the *b*-axis. Hence it may possibly be predicted that there is one Cu^{++} ion at the centre of this face. As in other copper salts, we may postulate that one Cu^{++} ion is situated at each corner of the unit cell and one at the centre of the (100) face. The closest distance between two copper ions for such an arrangement will be of the order of 5 Å being somewhat smaller than 5·5 and 6 Å found in other copper salts.

Regarding the surroundings of the Cu^{++} ions, we expect either a tetragonal or rhombic component superimposed on the cubic field. The field here is likely to be rhombic as each Cu^{++} ion is situated at the centre of an irregular octahedran formed by the two oxalate ions, the two ammonium ions and the two water molecules. The two water molecules may be co-ordinated and it is the two positively charged ammonium ions that are likely to be pulled apart by the large repulsive force exerted between them, and the similarly charged Cu^{++} ion. Hence the longest axis in this octahedran may be chosen as that passing through the two ammonium ions and the Cu^{++} ion at the centre.

Further discussion of the direction of this axis, and the nature and positions of the crystalline field with regard to the '*g*' values is deferred to till the complete investigation of the isomorphous cupric-potassium-oxalate crystal is made.

CUPRIC-FORMATE TETRAHYDRATE

Paramagnetic resonance of this in powder form has been studied by Lancaster and Gordy (1951). The '*g*' value = 2·2 and $\Delta H_{\frac{1}{2}} = 500$ gauss as compared with $g = 2{\cdot}2$ and $\Delta H_{\frac{1}{2}} = 400$ gauss obtained in the present

investigation. J. Uebersfeld (1953) has reported the 'g' value as 2·15 and $\Delta H_{\frac{1}{2}}$ as 230 gauss for cupric-formate in powder form. But it has not been stated whether it is tetrahydrate or dihydrate. A brief report on single crystals of both cupric-formate dihydrate and tetrahydrate has been given by H. Abe (1953) and it has been mentioned that the 'g' value varies from 2·06 to 2·32. A detailed study of the anisotropy of 'g' value and 'line-width' in two different planes of cupric formate tetrahydrate, has been taken up in the present investigation.

The crystals obtained were monoclinic and the faces belong to the forms c (001), m (110), ω' ($\bar{1}\bar{1}$1), and rarely 0 (111), and b (010). There is perfect cleavage along c (001).

Orientation 1. The formate crystal is placed with the b-axis along the magnetic field, with the (001) plane vertical.

The 'g' value varies from 2·1 to 2·19 and the polar diagram showing the anisotropy of line-width is shown in Fig. 8.

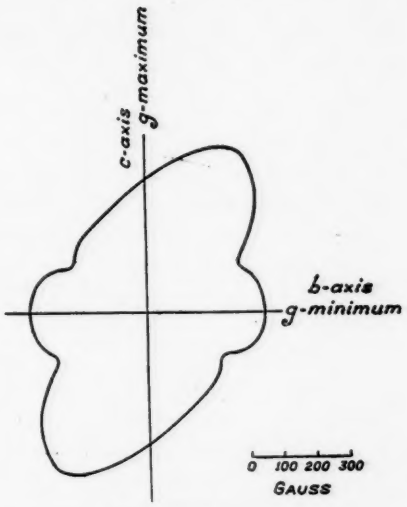

FIG. 8. Anisotropy of line-width in the (100) plane of Cupric-Formate-Tetrahydrate Crystal.

Orientation 2. The anisotropy was studied in the (001) plane with the b-axis along the magnetic field at start. In each case the measurements were taken at intervals of 10° each.

The 'g' value varies from 2·09 to 2·28 in this plane. The theoretical curve showing the variation of 'g' is shown in Figure 9, with the experimentally obtained points marked therein.

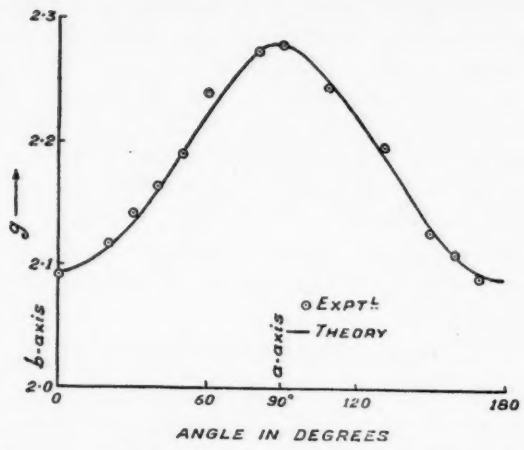

FIG. 9. Anisotropy of 'g' value in the (001) plane of Cupric-Formate-Tetrahydrate Crystal.

The polar diagram revealing the anisotropy of line-width in this plane is shown in Fig. 10.

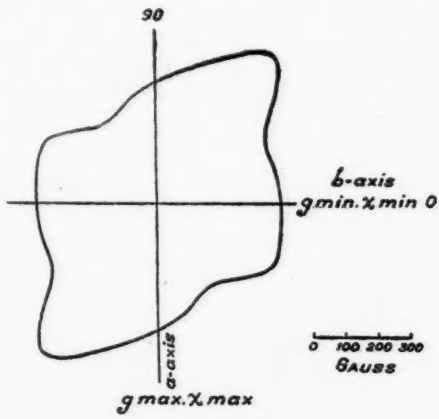

FIG. 10. Anisotropy of line-width in the (001) plane of Cupric-Formate-Tetrahydrate Crystal.

Cupric-formate tetrahydrate—$Cu(HCO_2)_2\,4\,H_2O$, is monoclinic and it is known that it contains two molecules per unit cell from the X-ray analysis of the same (Kabraji, 1931). According to Kabraji, the space-group of the crystal determined by Laue photographs is C_{2h}^3. The lattice is c-face centred and the unit cell contains only two molecules with the molecules

possessing the requisite symmetry in order to conform to the given space-group.

The cell dimensions are given as

$$a : b : c = 1{\cdot}0036 : 1 : 0{\cdot}7739.$$

$$a = 8{\cdot}156 \text{ Å}u; \quad b = 8{\cdot}128 \text{ Å}u; \quad c = 6{\cdot}290 \text{ Å}u; \quad \beta = 101° 5'.$$

The Cu^{++} ions occupy the eight corners and the centres of the (001) faces thus giving two molecules per unit cell.

Each Cu^{++} ion is surrounded by six-oxygen atoms, four of which belong to the four water molecules, the other two being those of the formate group. As in other cupric salts, it is expected here also, that the octahedral arrangement of the oxygen atoms is not quite regular, the four oxygen atoms of the water molecules forming a square, the other two being placed one above and the other right below. It is as if the octahedran is pulled out along the diagonal joining the oxygen atoms of the formate group. So we expect a mild tetragonal field superimposed on the relatively strong cubic field around the Cu^{++} ion. It is found that the longest diagonal of the octahedran occurs in the (*a*-*c*-) plane and magnetic resonance shows that the '*g*' value is also maximum in this plane.

The line of closest packing of Cu^{++} ions in the (001) plane makes an angle of about 46° with the *b*-axis. Hence the line-width is expected to be maximum in that direction. This is so in the present measurements (Fig. 10). The line-width is maximum and is 590 gauss in a direction making an angle of about 50° with the *b*-axis in the (001) plane.

Cupric-Butyrate Monohydrate $Cu(CH_3CH_2CH_2COO)_2 H_2O$

No resonance was observed in the region of 3 cm. working within a magnetic field range of 0 to 4500 gauss. Work at higher field-strengths and frequencies is necessary to find whether the substance behaves anomalously like copper acetate (Bleaney and Bowers, 1952) and copper propionate (Abe, 1953). The crystal structure of this seems to be complicated with 32 molecules per unit cell (Iball, 1947). Further work on this substance is in progress.

Summary

This paper is a report of the study of the paramagnetic resonance spectra of six cupric salts. Data for cupric-oxalate, cupric-sodium-oxalate, cupric-potassium-oxalate and cupric-ammonium-oxalate in the powder form have been obtained. Single crystals of cupric-ammonium-oxalate dihydrate and

cupric-formate tetrahydrate have been investigated for anisotropy of 'g' value and line-widths. No resonance was observed in cupric-butyrate monohydrate in the magnetic field ranging from 0 to 4500 gauss in the region of 3 cm. Structure of the crystals are discussed in relation to the magnetic properties of the same.

ACKNOWLEDGEMENT

The author takes this opportunity of recording her grateful thanks to Professor R. S. Krishnan for his interest and encouragement throughout the course of this investigation. Her thanks are also due to Dr. G. Suryan for suggesting the problem and helpful discussions and to Dr. R. V. G. Sundara Rao, for kindly determining the cell dimensions and the number of molecules per unit cell of the cupric-ammonium oxalate crystal by X-ray analysis at her request.

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RAMAN SPECTRUM OF CESIUM BROMIDE

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1. Introduction

The Raman spectra of a few alkali halides have in recent years been examined in detail by a number of investigators [Menzies, A. C. and Skinner, J. (1948 *a*, *b*), Krishnan, R. S. (1947), Krishnan and Narayanan, P. S. (1948) and Welsh *et al.* (1949)] in view of their importance for a proper understanding of the nature of the vibration spectra of these alkali halides in particular and that of crystals in general. Yet all these have been of the NaCl lattice type and so far no crystal of the body centred lattice type, *i.e.*, CsCl structure* has been experimentally investigated and any new data on such crystals are all the more valuable because of the opposing views which prevail concerning the vibration spectra of crystals. Some preliminary observations on the Raman spectrum of cesium bromide are therefore presented here.

2. Experimental Details

Cesium bromide which crystallises with CsCl structure is being grown synthetically by a few companies and in the present study two specimens were employed, one of which was supplied by Messrs. Harshaw Chemical Co., U.S.A., and the other was presented to Prof. R. S. Krishnan by Dr. Menzies, Research Director of Adam Hilger Ltd. The specimen from Harshaw Chemical Co. was of size 3 cm. × 2 cm. × ·5 cm. while the one from Hilger was about 5 cm. × 3 cm. × 2 cm. and clearer and more transparent than the former.

The spectra were recorded using as exciter the λ 2537 radiation from a quartz arc designed for this purpose. The experimental arrangement was such that the crystal could be placed close to the arc without the former getting heated and its polish getting spoiled. As in the case of the earlier studies on the spectra of alkali halides carried out in this laboratory, cesium bromide also was studied employing two spectrographs, *viz.*, the medium quartz spectrograph with a dispersion of about 140 $cm.^{-1}$ in the λ 2537 region and a large Littrow quartz spectrograph (E1) with a dispersion of 40 $cm.^{-1}$

* Although NH_4Cl and NH_4Br have CsCl structure, as the lattice points are occupied by NH_4 group rather than a single ion, they are not taken into consideration for this statement.

in the same region. With the smaller instrument and using a slit width of ·03 mm. it was found possible to obtain satisfactory spectra in about an hour while with the E 1 spectrograph and the same slit width an exposure of the order of 2 days was necessary. The spectra were measured with a cross-slide micrometer having an accuracy of ·0001 cm. and it was possible to measure the frequency shifts of the intense lines with an accuracy of 2 cm.$^{-1}$

An attempt was made to study the polarisation of the Raman spectrum using a collimated beam of unpolarised incident radiation but owing to the feebleness of the spectrum it was not possible to obtain any result even with an exposure of 5 days. Consequently the arc was kept close to the crystal and the condensing system dispensed with. Although the incident beam had now a wide angle of convergence determined only by the critical angle, it can easily be seen that even in spectra obtained in this manner it should be possible to identify lines with depolarisation less than 0·2 or 0·3 (Menzies and Skinner, *loc. cit.*). Yet no line could be definitely stated to be polarised to this extent and all the observed Raman lines were depolarised. Consequently a more accurate experimental measurement with collimated incident beam is being tried again with some improvements.

3. Results and Discussion

The observed spectrum, as is to be expected because of the large masses of the constituent atoms, is restricted to the region of very small frequency shifts and as such a prerequisite to any satisfactory observation of either the frequency shift and the intensity distribution is efficient filtering of the exciting radiation from the scattered light. Figures 1 and 3 on Plate XIII show the spectrum of cesium bromide taken with the large and the medium spectrographs respectively, while Figs. 2 and 4 on the same plate represent the corresponding microphotometer records. One can easily identify five Raman lines in the recorded spectrum in spite of their being slightly broad and diffuse and the observed frequency shifts are given in Table I. The frequency shifts have also been marked in the figures. As will be seen in more detail later, the reason for the apparent diffuseness is a crowding together of a large number of lines which differ in frequency from one another by only very small amounts.

The figures within brackets by the side of the frequency shifts indicate roughly the relative intensity of the Raman lines. In the most intense spectrograms taken, there are indications of the existence of a spectrum in the region beyond 190 cm.$^{-1}$ up to 220 cm.$^{-1}$ although it is extremely weak. There is evidence also for the presence of lines in the spectrum in the region of 30 to 50 cm.$^{-1}$ but owing to the halation caused by λ 2537 and the spurious

TABLE I

Raman spectrum of cesium bromide

Observed frequency shift in cm.$^{-1}$	Assignment	Calculated frequency in cm.$^{-1}$
79 (5)	ν_2, $\nu_5+\nu_7$	80
107 (4)	$2\nu_5$	108
135 (10)	$2\nu_3$	136
155 (1)	$2\nu_2$	156
190 (1)	$2\nu_1$	190

band in this region it was not possible to measure these. An accurate measurement of the intensity distribution in the entire spectrum is being carried out.

So far the only theoretical consideration of the frequencies of vibration of CsCl structure on the basis of the Born model is that of Krishnan and Roy (1952); even they have calculated explicitly only that of one mode, *viz.*, that in which the cesium lattice oscillates as a whole against that of bromine. On the other hand, according to Prof. Raman (1943, 1947), the cesium chloride structure which consists of two simple cubic lattices interpenetrating in such a manner that the atoms of one lattice are located at the body centres of the cubic lattice formed by the other has only 11 distinct normal modes of vibration (Chelam, 1943) all of which are inactive as fundamentals in light scattering. Exact expressions for these 11 discrete normal vibrations have also been worked out (K. G. Ramanathan, 1947) in terms of 12 force constants which take account of the influence of the 26 nearest neighbours of every atom. A considerable reduction in the number of force constants can be effected once certain simplyfying assumptions are made. But they lead to a reduction of the number of distinct frequencies also from 11 to 7 and simplified formulæ for these 7 frequencies have also been given in terms of 4 independent constants only which are again connected by an additional relation. Consequently it is possible to evaluate roughly the frequencies of the various modes if one can identify in the spectrum three frequency shifts. For this it will be advantageous to consider first the activity of the different modes in second order scattering along lines dealt with in detail by Prof. Raman (1947 *a*, *b*). Since the two

TABLE II

Sl. No.	Degeneracy	Description of mode	Direction of oscillation	$4\pi^2\nu^2c^2$	Frequency	Frequency in cm.$^{-1}$ calculated	Theoretical 2nd order activity
I	6	(011) Plane	(011) or (011)	$\frac{P-2T}{m_1}+\frac{P'-2T'}{m_2}+\frac{4(T+T')}{m_1+m_2}$	ν_1	82	Very weak
II	3	Two lattices	Arbitrary	$\frac{P+2T}{m_1}+\frac{P'+2T'}{m^2}$	ν_2	78	Weak
III	3	(III) Br ions	,,	$(P'-2T')/m_2$	ν_3	68	Very strong
IV	3	(100) ,,	Normal	,,	ν_3		Weak
V	3	(011) ,,	(100)	$(P'+2T')/m_2$	ν_4	58	Weak
VI	6	(100) ,,	Taugential	,,	ν_4		Weak
VII	3	(111) Cs ions	Arbitrary	$(P-2T)/m_1$	ν_5	54	Strong
VIII	3	(100) Cs ions	Normal	,,	ν_5		Weak
IX	3	(011) ,,	(100)	$(P+2T)/m_1$	ν_6	45	Weak
X	6	(100) ,,	Tangential	,,	ν_6		Weak
XI	6	(011) Plane	(011) or (011)	$-\frac{4(T+T')}{m_1+m_2}$	ν_7	26	Very weak

interpenetrating lattices in the structure of cesium bromide consist of dissimilar particles, their oscillation against each other (mode II in Table II) is necessarily active in infra-red absorption and as has been done by Krishnan and Roy (*loc. cit.*) can be identified with the infra-red absorption at 134 μ (Barnes, 1932). Therefore, the observed frequency shift of 155 cm.$^{-1}$ in the second order Raman spectrum obviously corresponds to the octave of mode II. Of the remaining modes, modes III and VII involve appreciable changes in the relative distances of the Cs and Br ions, and the octaves of these are therefore to be expected to appear with considerable intensity, that involving a movement of the Br ions only being stronger because of the larger refractivity. Further ratio of the frequencies of these two modes should be roughly proportional to the square root of inverse ratio of the masses of the ions. Therefore, one can take the observed second order lines 135 cm.$^{-1}$ and 107 cm.$^{-1}$ to represent the octaves of modes III and VII respectively.

The force constants P, P′, T, and T′ are now easily calculated using for ν_2, ν_3 and ν_5 the values 78, 68, 54 cm.$^{-1}$ in formulæ given in Table II and utilising the relation $P + 2T = P' + 2T'$. They are given by

$$P = 2{\cdot}02 \times 10^4 \text{ dynes/cm.} \quad P' = 1{\cdot}97 \times 10^4 \text{ dynes/cm.}$$

$$T = -\,{\cdot}12 \times 10^4 \text{ dynes/cm.} \quad T' = -\,{\cdot}09 \times 10^4 \text{ dynes/cm.}$$

and the other frequencies calculated using these force constants are also included in Table II. The rough theoretical second order activity to be expected is also indicated in the same Table II. As mentioned earlier the approximations made in the calculation lead to a reduction in the number of distinct frequencies and even these are very close to each other. While these themselves are adequate to explain in a satisfactory manner the observed features of the second order spectrum, a more rigorous calculation of all the 11 frequencies will give a better account of the width and intensity of the second order lines. A very striking feature of the spectrum is the high intensity of the Raman line at 79 cm.$^{-1}$ which has been attributed to the combination of modes VII and IX, *i.e.*, the frequency $\nu_5 + \nu_7$. A possible reason for this is that it is very nearly equal to the frequency of mode II and consequently results in an appreciable activity of both due to this accidental coincidence. The extremely faint line at 190 cm.$^{-1}$ is probably the octave of ν_1. The assignment of the observed Raman lines on the basis of the frequencies given in Table II is also indicated in Table I. However, it will be evident that though only a few of the theoretically allowed octaves and combinations which comprise the second order spectrum have been found essential to explain the prominent frequency shifts it is necessary to consider in detail

all of them and their activity in second order Raman effect for a quantitative explanation.

In conclusion the author wishes to express his grateful thanks to Prof. R. S. Krishnan for his kind interest and constant encouragement.

SUMMARY

The Raman spectrum of cesium bromide, which crystallises with CsCl structure, has been studied using the resonance radiation of mercury as exciter. It consists of a number of lines very close to the exciting line of which five prominent frequency shifts are 79, 107, 135, 155 and 190 cm.$^{-1}$ A calculation of the 7 distinct frequencies of CsBr using the approximate formulæ worked out by K. G. Ramanathan on the basis of Raman's theory has been carried out and an attempt made to explain the prominent features of the observed spectrum.

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FIG. 2

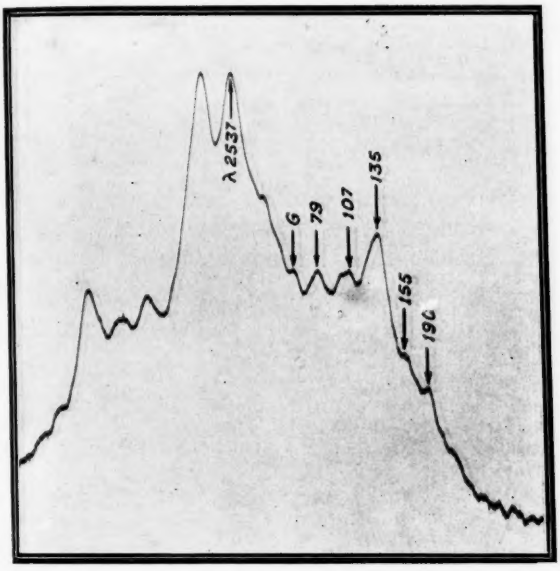

FIG. 4

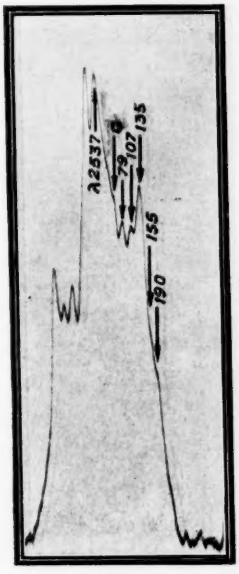

FIG. 1

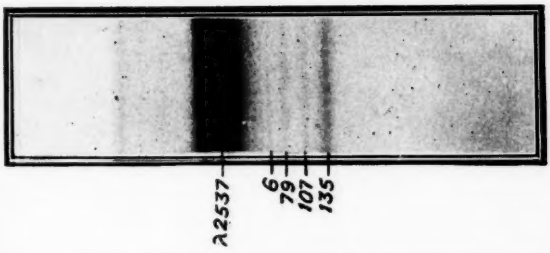

FIG. 3

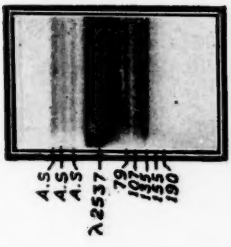

FIG. 1. Raman Spectrum of Cesium Bromide taken with E 1 Quartz Spectrograph.
FIG. 2. Microphotometer record of Spectrum taken with E 1.
FIG. 3. Raman Spectrum of Cesium Bromide taken with medium Quartz Spectrograph.
FIG. 4. Microphotometer record of picture recorded with the medium Spectrograph.

GENERALIZATION OF NORMAL CURVATURE OF A CURVE IN A RIEMANNIAN V_n

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1. The object of the present paper is to define an invariant which is a generalization of the expression for the normal curvature of a curve in V_n, and to obtain generalizations of some known results.

2. Consider a Riemannian space V_n of co-ordinates x^i, $i = 1, 2, \ldots n$ and metric

$$ds^2 = g_{ij}dx^i dx^j \quad , \tag{2.1}$$

imbedded in a V_{n+1} of co-ordinates y^α, $\alpha = 1, 2, \ldots n+1$ and metric

$$ds^2 = a_{\alpha\beta}dy^\alpha dy^\beta. \tag{2.2}$$

We have the relation

$$g_{ij} = a_{\alpha\beta}y^\alpha{}_{,i}y,^\beta{}_j \quad , \tag{2.3}$$

where comma denotes covariant differentiation.

Let N^α denote the contravariant components of the unit normal to V_n, then

$$a_{\alpha\beta}N^\alpha N^\beta = 1, \tag{2.4}$$

and

$$a_{\alpha\beta}N^\alpha y^\beta{}_{;i} = 0, \ (i = 1, 2, \ldots n) \tag{2.5}$$

where (;) followed by an index denotes generalized covariant derivative (or tensor derivative) with respect to the x with that index.

We have

$$N^\alpha{}_{;i} = -\ \Omega_{ij}g^{jk}y^\alpha{}_{,k} \quad , \tag{2.6}$$

where Ω_{ij} are the components of a symmetric covariant tensor of the second order given by

$$\Omega_{ij} = y^\alpha{}_{;ij}a_{\alpha\beta}N^\beta. \tag{2.7}$$

From (2.6) we have

$$N^{\alpha}{}_{;i}e^{i} = -\, e^{i}\Omega_{ij}g^{jk}y^{\alpha}{}_{,k} \quad , \tag{2.8}$$

where e^{i} are the components of a unit vector in the hypersurface.

The resolved part of the derived vector $N^{\alpha}{}_{;i}e^{i}$ in the direction of another unit vector **a** in the hypersurface is given by

$$\begin{aligned}(-\, e^{i}\Omega_{ij}g^{jk}y^{\alpha}{}_{,k})\, a_{\alpha\beta}\,(y^{\beta}{}_{,l}a^{l}) &= -\, e^{i}\Omega_{ij}g^{jk}g_{kl}a^{l} \\ &= -\, \Omega_{ij}e^{i}a^{j},\end{aligned} \tag{2.9}$$

and therefore the resolved part of the derived vector $N^{\alpha}{}_{;i}e^{i}$ along e^{i} is $-\, \Omega_{ij}e^{i}e^{j}$. (2.10)

3. Let λ^{α} be the components of a unit vector in the direction of a curve of a congruence such that one curve of the congruence passes through each point of V_n.

λ^{α} can be expressed in terms of $y^{\alpha}{}_{,i}$ and N^{α} as

$$\lambda^{\alpha} = y^{\alpha}{}_{,i}t^{i} + rN^{\alpha}. \tag{3.1}$$

Since λ^{α} are the components of a unit vector,

$$\begin{aligned}1 \equiv a_{\alpha\beta}\lambda^{\alpha}\lambda^{\beta} &= a_{\alpha\beta}\,(y^{\alpha}{}_{,i}t^{i} + rN^{\alpha})\,(y^{\beta}{}_{,j}t^{j} + rN^{\beta}) \\ &= g_{ij}t^{i}t^{j} + r^{2}.\end{aligned} \tag{3.2}$$

The tensor derivative of (3.1) with respect to x^{j} yields

$$\begin{aligned}\lambda^{\alpha}{}_{;j} &= y^{\alpha}{}_{;ij}t^{i} + y^{\alpha}{}_{;i}t^{i}{}_{;j} + rN^{\alpha}{}_{;j} + r_{;j}N^{\alpha} \\ &= N^{\alpha}\,[\Omega_{ij}t^{i} + r_{;j}] + y^{\alpha}{}_{,k}\,[t^{k}{}_{;j} - r\Omega_{ij}g^{ik}]\end{aligned} \tag{3.3}$$

From (3.3) we have

$$\begin{aligned}&a_{\alpha\beta}\left(y^{\beta}{}_{,l}\,\frac{dx^{l}}{ds}\right)\left(\lambda^{\alpha}{}_{;j}\,\frac{dx^{j}}{ds}\right) \\ &\qquad = -\,[r\Omega_{lj} - t_{l;j}]\,\frac{dx^{l}}{ds}\,\frac{dx^{j}}{ds}.\end{aligned} \tag{3.4}$$

If the congruence be one of normals to the hypersurface, then $t^{i} = 0$, $r = 1$, and the right-hand member of (3.4) reduces to (2.10). The expression

$$(r\Omega_{lj} - t_{l;j})\,\frac{dx^{l}}{ds}\,\frac{dx^{j}}{ds}$$

may therefore be considered as a generalization of the normal curvature of the curve whose unit tangent has components dx^i/ds. We shall call it the *generalized normal curvature of the curve relative to the congruence.* This quantity depends only on the direction of the curve C at the point considered, and is the same for all curves tangent to C at the point. We may therefore call it the *generalized normal curvature of the hypersurface relative to the congruence for the given direction.*

4. *Generalization of Dupin's Theorem on normal curvature.* If e^i are the components in the x's of a unit vector e at a point P in V_n, the generalized normal curvature of the hypersurface at P in the direction of e has the value

$$k_\lambda = (r\Omega_{lj} - t_{l;j})\, e^l e^j. \tag{4.1}$$

Consequently if $\mathbf{e}_{h1}$ $(h = 1, 2, \ldots . n)$ are the unit tangents at P to the curves of an orthogonal ennuple in V_n, the sum of the generalized normal curvatures of V_n for the directions of the ennuple is

$$\sum_h (r\Omega_{ij} - t_{i;j})\, e^i{}_{h1} e^j{}_{h1} = (r\Omega_{ij} - t_{i;j})\, g^{ij}. \tag{4.2}$$

Since the expression on the right is an invariant, we have the theorem: *The sum of the generalized normal curvatures of a hypersurface V_n relative to a given congruence, for* n *mutually orthogonal directions at a point is invariant and is equal to* $(r\Omega_{ij} - t_{i;j})g^{ij}$. This sum may be called *the mean generalized curvature of the hypersurface* at the point considered, relative to the given congruence. We shall denote it by M_λ. Thus

$$\mathrm{M}_\lambda = (r\Omega_{ij} - t_{i;j})\, g^{ij} \tag{4.3}$$

If the congruence be one of normals to the hypersurface we have the known result:

The sum of the normal curvatures of a hypersurface V_n for n *mutually orthogonal directions at a point is invariant and equal to* $\Omega_{ij}g^{ij}$ (Weatherburn, 1950).

From the definition of the generalized normal curvature it also follows that *the generalized normal curvature of a hypersurface for any direction is the negative tendancy of the unit tangent to the curve of the congruence through the point in that direction.* But the sum of the tendancies of λ for n mutually orthogonal directions in V_n is equal to $div_n\lambda$.

Hence

$$M_\lambda = - div_n \lambda, \tag{4.4}$$

which may be stated as follows:

The mean generalized curvature of a hypersurface relative to a given congruence at any point is equal to the negative of the divergence of the unit tangent to the curve of the congruence through the point.

If the congruence be one of normals to the hypersurface, we have the known result:

The mean curvature of a hypersurface is equal to the negative of the divergence of the unit normal (Weatherburn, 1950).

5. *Principal generalized curvatures. Lines of generalized curvature.*

The generalized normal curvature of V_n for a variable direction **p** is given by

$$k_\lambda = \frac{(r\Omega_{ij} - t_{i;j})\, p^i p^j}{g_{ij} p^i p^j} . \tag{5.1}$$

The stationary values of k_λ are those determined by the directions for which

$$\frac{dk_\lambda}{dp^j} = 0 \,(j = 1, 2, \ldots . n).$$

Writing (5.1) in the form

$$(r\Omega_{ij} - t_{i;j})\, p^i p^j - k_\lambda g_{ij} p^i p^j = 0$$

and differentiating with respect to p^j, we see that the directions corresponding to the maximum and minimum values of k_λ are those which satisfy the equations

$$[r\Omega_{ij} - \tfrac{1}{2}(t_{i;j} + t_{j;i}) - k_\lambda g_{ij}]\, p^i = 0 \tag{5.2}$$

and the maximum and minimum values of k_λ are the roots of the equation

$$| r\Omega_{ij} - \tfrac{1}{2}(t_{i;j} + t_{j;i}) - k_\lambda g_{ij} | = 0 \tag{5.3}$$

The directions satisfying (5.2) are the principal directions in V_n determined by the symmetric part of the covariant tensor $(r\Omega_{ij} - t_{i;j})$. We shall therefore call the directions determined by (5.2) as the *principal generalized directions*, and the maximum and minimum values of (5.1) [which are the generalized curvatures of V_n in the principal generalized directions and are the roots of the equation (5.3)] as the *principal generalized curvatures*. A curve whose

direction at each point is a principal generalized direction is a *line of generalized curvature* in V_n. There are thus n congruences of lines of generalized curvature in V_n corresponding to a given congruence λ in V_n. If the roots of (5.3) are all simple, the principal generalized directions relative to a given congruence are uniquely determined and are mutually orthogonal. Corresponding to a multiple root of order m it is possible in a multiply-infinite number of ways, to choose m mutually orthogonal principal generalized directions. These are orthogonal to the principal generalized directions determined by the other roots of (5.3). Also the principal generalized directions satisfy the equations

$$[r\Omega_{ij} - \tfrac{1}{2}(t_{i;j} + t_{j;i})]\, p^i{}_{h|} p^j{}_{k|} = 0 \,(h \neq k) \tag{5.4}$$

Let $\mathbf{e}_{h|}$ be the unit tangents to the n congruences of lines of generalized curvature. Then the principal generalized curvatures are given by

$$k_{\lambda|h} = (r\Omega_{ij} - t_{i;j})\, e^i{}_{h|} e^j{}_{h|}, \; (h = 1, 2, \ldots . n), \tag{5.5}$$

Any other unit vector $\mathbf{a}$ in V_n is expressible in the form

$$\mathbf{a} = \sum_h \mathbf{e}_{h|} \cos \alpha_h \tag{5.6}$$

where

$$\cos \alpha_h = \mathbf{a} \cdot \mathbf{e}_{h|} = a^i e_{h|i} \quad ,$$

a^i being the contravariant components of $\mathbf{a}$ and α_h being the inclination of $\mathbf{a}$ to $\mathbf{e}_{h|}$. The generalized normal curvature of V_n for the direction of $\mathbf{a}$ relative to the congruence is given by

$$k_\lambda = (r\Omega_{ij} - t_{i;j})\, a^i a^j \quad ,$$

Substituting in the second member the values of a^i corresponding to (5.6) we obtain,

$$k_\lambda = \sum_h k_{\lambda|h} \cos^2 \alpha_h. \tag{5.7}$$

The sum of the principal generalized curvatures, being the sum of the generalized normal curvatures for n mutually orthogonal directions in V_n, is equal to the mean generalized curvature.

Thus

$$\sum_h k_{\lambda|h} = \mathrm{M}_\lambda = - \, div_n \lambda. \tag{5.8}$$

For the congruence of normals to V_n, the principal generalized directions, the principal generalized curvatures, and the lines of generalized curvature

are the principal directions, the principal curvatures, and the lines of curvature respectively. In this case (5.7) reduces to Euler's formula for the normal curvature of a hypersurface V_n imbedded in V_{n+1} (Weatherburn, 1950).

6. *Generalized conjugate directions and generalized asymptotic directions.* The directions of two vectors, **a** and **b**, at a point in V_n, may be said to be *generalized conjugate* relative to a congruence of curves in V_{n+1} if

$$[r\Omega_{ij} - \tfrac{1}{2}(t_{i;j} + t_{j;i})]\, a^i b^j = 0 \tag{6.1}$$

and two congruences of curves in the hypersurface may be said to be generalized conjugate relative to a congruence of curves in V_{n+1} if the directions of the two curves through any point are generalized conjugate. It follows from (5.4) that *the principal generalized directions at a point of a hypersurface are generalized conjugate.*

Also we have the following more general theorem:

A vector at a point of a hypersurface V_n, whose components are linear combinations of the components of p *vectors tangent to lines of generalized curvature relative to a given congruence in V_n, is generalized conjugate to the vector whose components are linear combinations of the remaining* n–p *vectors tangent to lines of generalized curvature.*

For the congruence of normals to the hypersurface these reduce to the following known results:

1. *The directions of two lines of curvature at a point of a hypersurface are conjugate.*

2. *A vector at a point of a hypersurface whose components are linear combinations of the components of* p *vectors tangent to the lines of curvature is conjugate to the vector whose components are linear combinations of the remaining* n–p *vectors tangent to lines of curvature* (Eisenhart, 1949).

A direction in V_n, which is generalized self-conjugate, is said to be *generalized asymptotic.* Thus the condition that the direction of the vector **a** at a point of V_n be generalized asymptotic is

$$[r\Omega_{ij} - \tfrac{1}{2}(t_{i;j} + t_{j;i})]\, a^i a^j = 0,$$

which may be put in the form

$$(r\Omega_{ij} - t_{i;j})\, a^i a^j = 0. \tag{6.2}$$

A generalized asymptotic line in a hypersurface relative to a given congruence in V_{n+1} is a curve, whose direction at every point is generalized asymptotic. The differential equation of such a line is

$$(r\Omega_{ij} - t_{i;\,j})\, dx^i dx^j = 0. \tag{6.3}$$

From (6.2) and (4.1) it follows that *the generalized normal curvature* of a *hypersurface in a generalized asymptotic direction is zero.* Relative to the congruence of normals to the hypersurface, the generalized conjugate directions are the conjugate directions and the generalized asymptotic directions reduce to asymptotic directions.

From (3.3) we see that if **a** and **b** be unit vectors in V_n, the resolved part along **b** of the derived vector of $\boldsymbol{\lambda}$ along **a** is

$$-\,[r\Omega_{ij} - t_{i;j}]\, a^i b^j \tag{6.4}$$

Using (6.1) and (6.4) we find that a pair of generalized conjugate directions in V_n relative to a congruence in V_{n+1} is such that *the resolved part in one direction of the derived vector of the unit tangent to the congruence in the other direction is the negative of the resolved part in the second direction, of the derived vector of the unit tangent to the congruence in the first direction.* For the particular case in which the direction is generalized self-conjugate, we may state the theorem as follows:

The derived vector of the unit tangent to a congruence in V_{n+1} along a curve of the hypersurface will be orthogonal to the curve provided the curve be a generalized asymptotic line in the hypersurface, relative to the congruence.

If the congruence be one of normals to V_n, these reduce to the following known results:

1. *Conjugate directions in a hypersurface are such that the derived vector of the unit normal in either direction is orthogonal to the other direction* (Weatherburn, 1950).

2. *The derived vector of the unit normal along a curve of the hypersurface will be orthogonal to the curve provided the curve be an asymptotic line in the hypersurface* (Weatherburn, 1950).

Summary

In the present paper a congruence of curves through points of a hypersurface V_n imbedded in a Riemannian V_{n+1} has been considered. In analogy with the normal curvature of a curve C in V_n, the generalized normal curvature of C at any point of it, relative to the curve of the congruence through

that point, has been defined as the negative of the resolved part along C, of the derived vector of the unit tangent to the curve of the congruence through the point along C. The concepts of normal curvature of a hypersurface, principal directions, principal curvatures, lines of curvature, conjugate directions, asymptotic directions and asymptotic lines have been generalized and generalizations of several known theorems on the curvature of a hypersurface V_n in V_{n+1} have been obtained.

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SPECTROPHOTOMETRIC ESTIMATION OF THORIUM BY MORELLIN

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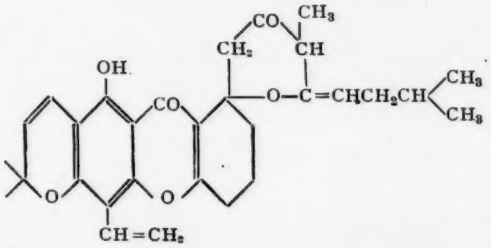
Spectrophotometric determination of thorium has not received much attention so far.[1] Thomason, Parry and Byerly[2] suggested a spectrophotometric method, employing 1-(0-arsonophenylazo)-2-naphthol-3, 6-disulphonic acid, known as " apans " or " thorin " as a complex forming reagent with thorium. The method is not applicable in presence of rare earths, titanium, zirconium and iron. Mayer and Bradshaw[3] used the reagent for the determination of thorium in magnesium base alloys while Banks and Byrd[4] employed it for the estimation of thorium in monazite. Recently, Moeller and Tecotzky[5] used naphthazarin while Purushottam[6] employed quinalizarin for the estimation of microquantities of thorium in its pure solution. In view of the small number of colorimetric reagents applicable to thorium, Moeller and Tecotzky[5] suggested that any potentially useful colorimetric reagent is of general interest in the spectrophotometric estimation of thorium.

Morellin, a plant pigment, occurring in the pericarp of the seeds of *Garcenia morella*, was isolated by Rao.[7] Rao *et al.*[8] suggested the structural formula



Morellin has a chelate group[9] C, C, C—O, OH, which can be expected to form inner complexes with metal ions. Thorium forms an orange-red complex with morellin in an alcoholic solution. The colour of the complex does not fade even on keeping the solution for several days. An investigation was, therefore, conducted to utilise this reaction for quantitative estimation of thorium and also to determine the composition of the coloured complex spectrophotometrically.

EXPERIMENTAL

Reagents

(*a*) Thorium nitrate solution: Thorium nitrate (B.D.H.) was freed from common elements by the oxalic acid method and later from rare earths by precipitation with purified *m*-nitrobenzoic acid[10] at pH 3·2. The precipitate was washed, ignited and the thorium oxide dissolved in concentrated sulphuric acid and reprecipitated with dilute ammonium hydroxide solution. The precipitate obtained was dissolved in the minimum amount of dilute nitric acid, the excess acid removed and the nitrate further purified by crystallising thrice. The solid obtained was finally utilised to make up a stock solution in distilled water, the thorium content of which was determined by the sebacic acid method. The solution was further diluted with alcohol to get a strength of $1 \cdot 352 \times 10^{-3}$ M.

(*b*) Morellin solution: Morellin crystals, obtained through the courtesy of Dr. P. L. N. Rao, were purified by crystallising thrice from absolute alcohol, when shining orange-yellow needles (m.p. 156° C.), were obtained. Since morellin is insoluble in water, the crystals were dissolved in absolute alcohol to get a solution of $1 \cdot 352 \times 10^{-3}$ M (Mol. Wt. = 544).

Equimolar solutions of thorium and of morellin, having the concentration $1 \cdot 352 \times 10^{-3}$ M, were employed during this investigation, unless otherwise mentioned.

(*c*) Other reagents used during the course of these studies were of A.R. quality or purified in these laboratories.

Instruments

(1) Coleman model 14 universal spectrophotometer with purple filter 14-214 (PC-4) was used. The cuvettes (optical path = 1·58 cm.) were of 14-302 type of a special glass.

(2) pH measurements were made by the glass electrode with a Beckman pH meter.

Absorption spectra of morellin and thorium-morellin complex

1·5 ml. of the morellin solution was made up to 10 ml. with 50% alcohol. The absorption spectrum of this solution (50% alcohol as reference solution) is represented by the curve B (Fig. 1) which shows that the absorption maximum for morellin is at 410 mμ and also that the absorption is comparatively negligible between the wave-lengths 510 mμ and 600 mμ. Further studies showed that with the change in concentration of morellin, there was appreciable variation in the absorption at 410 mμ but it was very little between

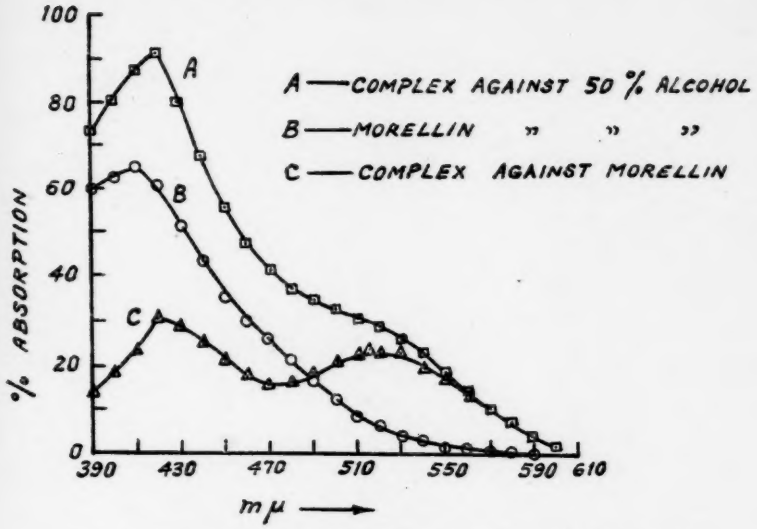


FIG. 1. Absorption spectra of thorium-morellin complex and morellin.

510 mμ and 600 mμ. The morellin solution in the concentration range 5 to 110 p.p.m. was also found to obey Beer's law at 410 mμ.

With 50% alcohol as reference solution, the absorption curve A (Fig. 1) was obtained for a mixture of 0·3 ml. of thorium solution and 1·5 ml. of morellin made up to 10 ml. with 50% alcohol. The shift in the absorption band towards longer wave-length in this case is due to the formation of thorium complex with morellin. Curve C (Fig. 1) is the absorption curve for the same solution, when morellin solution of the corresponding concentration was employed as reference solution. This curve shows two absorption maxima at 420 mμ and 515 mμ.

Since absorption by morellin solution is quite appreciable at 420 mμ the maximum of the complex at 515 mμ was chosen for all spectrophotometric studies on the complex.

Minimum amount of morellin necessary for the estimation of thorium

The optical densities (at 515 mμ) of a series of solutions having morellin to thorium ($1{\cdot}352 \times 10^{-4}$ M) ratio of 0·5 : 1 to 10 : 1 were determined. The results are presented in Fig. 2. The curve indicates that the optical density of the complex remains practically constant when the mole ratio of morellin to thorium is 5 and above. For subsequent studies, the mole ratio of the

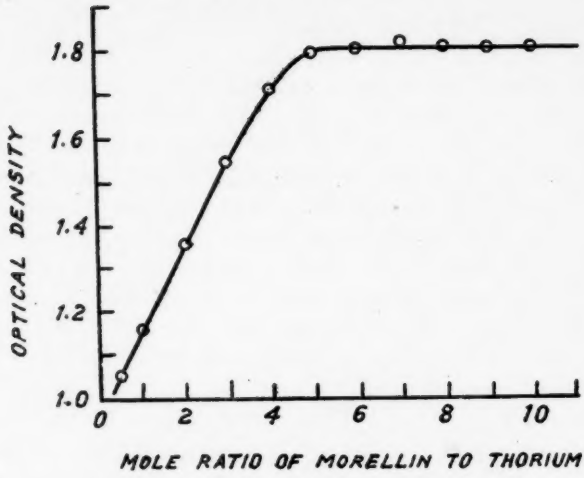


FIG. 2. Effect of the amount of the reagent.

reagent to thorium was, therefore, maintained at 5 or higher. Since the curve does not show a sharp break, it indicated that the complex undergoes dissociation in the medium employed, and hence this method does not give an idea of the composition of the complex. Other methods for determining the molar ratio of the reactants in the complex had to be tried.

Effect of concentration of alcohol on thorium-morellin complex during the estimation

When alcohol strength was below 40%, both the morellin and its complex with thorium get partially precipitated. At higher concentrations of alcohol (40–80%), precipitation of the reagent and the complex did not take place and the percentage transmission of the complex remained practically constant. In general, 50% alcohol was found to be a satisfactory medium for studies on the complex.

Effect of pH on thorium-morellin complex

Morellin is found to be pale orange-red in the alkaline medium and yellow in the acid range, the colour change of the indicator occurring at a pH of 7·2. The effect of pH on the complex as well as on morellin was studied to find out the suitable range of pH for the estimation of thorium, when the complex would be stable. As the common buffers were found to affect either the transparency or the stability of the complex solution, the pH had to be altered with 0·1 N solution of hydrochloric acid or sodium

hydroxide. The following conclusions were drawn from the absorption spectra obtained at different pH:

(i) The absorption maximum for morellin occurs at 410 mμ between pH 2·0 and 7·0. With the rise in pH beyond 7·2, the absorption maximum shifts to 430 mμ.

(ii) At a pH lower than 4·2, the addition of thorium solution to that of morellin does not produce any change in the absorption maximum of morellin (410 mμ), showing thereby that thorium complex is not formed in this pH range.

(iii) At a pH higher than 7·2, the absorption maximum of the complex shifts from 420 mμ to 430 mμ, thus overlapping with the absorption maximum of morellin in the alkaline pH. Hence it can be inferred that even in this pH range the complex is not formed.

(iv) Between pH 5 and 7, the complex has maximum stability and with morellin as reference solution, it gives two absorption maxima at 420 mμ and 515 mμ.

For the estimation of thorium, pH range of 5 to 7 was, therefore, employed. This pH range is obtained with neutral thorium nitrate solution in 50% alcohol.

Standard curve for the estimation of thorium

Maintaining a morellin to thorium mole ratio of 5, the complex solutions for various concentrations of thorium were prepared and their optical densities at 515 mμ indicated that Beer's law was obeyed at all concentrations between 1·4 to 25 p.p.m. of thorium.

Differential colorimetry for the estimation of thorium

Hiskey and co-workers[11–13] and Bastian and co-workers[14–15] used the coloured complex itself as the reference solution to improve the accuracy of the estimation even beyond Beer's law range. To verify this, a reference solution was prepared with a concentration of $9{\cdot}013 \times 10^{-5}$ M with respect to thorium, maintaining the mole ratio of morellin to thorium at 5. Using this solution, optical densities determined for a series of complex solutions of different concentrations, wherein the mole ratio of the reagent to the thorium was 5: 1, are given in Fig. 3. It shows that 60 p.p.m. of thorium can be estimated by this method.

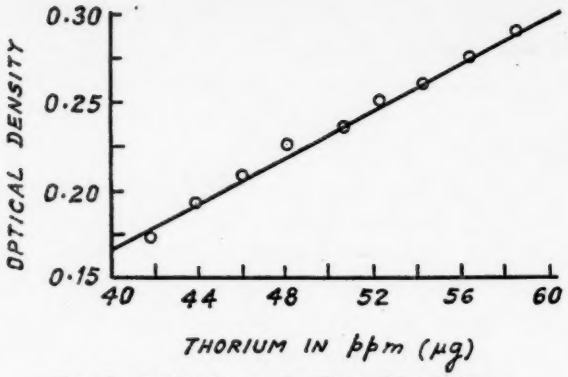


FIG. 3. Standard curve by differential colorimetry.

Interference of foreign ions

The stock solution of the complex was $1 \cdot 515 \times 10^{-4}$ M with respect to thorium, having a mole ratio of morellin to thorium as 6. 10 ml. of this solution was mixed with various quantities of foreign salts and the total volume made to 25 ml. with 50% alcohol. The concentration of the interfering salt was progressively increased till the optical density changed by 2% of the theoretical value. Thus the limiting concentration of the interfering salts was determined for more than 30 salts and the results are given in Table I.

Oxalate, iodate, phosphate, fluoride and carbonate of sodium, potassium or ammonium interfere even in traces as these anions precipitate thorium.

Molar composition of the complex

Since the mole ratio in the thorium-morellin complex could not be determined from the preceding data, trials were made by the method of continuous variations, proposed by Job[16] and modified by Vosburgh and Cooper.[17] X ml. of morellin solution ($1 \cdot 352 \times 10^{-3}$ M) were mixed with $(10 - x)$ ml. of thorium solution of the same molarity, and the value of x varied from 1 to 9. Optical densities of these mixtures were determined at 515 mμ, employing morellin as blank. The absorption due to the reacting components is negligible at 515 mμ. The Y function, defined as the difference between the optical density of the complex and of the corresponding components for no reaction, amounts, in this case, to the observed optical density for the complex. In Fig. 4, the values of Y for the mixtures of thorium and morellin in different proportions are plotted against x. The peak in the curve occurs, when the mole ratio of morellin to thorium is 8 : 2. The formula of

TABLE I

Foreign Ion	Salt	Ionic ratio tolerated foreign ion/Th^{++++}
Ag^{+}	Nitrate	> 5
Al^{+++}	,,	< 1
Ba^{++}	Chloride	2
Be^{++}	,,	> 5
Bi^{+++}	Nitrate	5
Ca^{++}	Chloride	> 5
Cd^{++}	Nitrate	> 5
Cr^{+++}	Sulphate	1
Ce^{+++}	Nitrate	7
Ce^{++++}	,,	< 1
Co^{++}	,,	< 1
Di^{+++} (Pr^{+++}, Nd^{+++}) ..	,,	7·5
Fe^{+++}	Chloride	< 1
Hg^{+}	,,	< 1
Hg^{++}	,,	2·5
K^{+}	,,	> 50
La^{+++}	Nitrate	8
Mg^{++}	Chloride	> 5
Mn^{++}	Nitrate	> 5
Na^{+}	Chloride	> 50
NH_4^{+}	,,	> 50
Pb^{++}	Nitrate	3
Sn^{++}	Chloride	1
Sr^{++}	,,	> 5
Ti^{++++}	Chloride	1
UO_2^{++}	Nitrate	< 1
Zn^{++}	Chloride	> 5
Zr^{++++}	Nitrate	1
AsO_4^{-}	Sodium	< 1
Br^{-}	Potassium	> 50
Cl^{-}	,,	> 50
CNS^{-}	,,	2
CrO_4^{--}	,,	5
$Fe(CN)_6^{----}$	,,	< 1
I^{-}	,,	> 50
MnO_4^{-}	,,	1
NO_3^{-}	Sodium	> 50
SO_4^{--}	,,	< 5
VO_4^{---}	,,	< 1
WO_4^{--}	,,	< 1

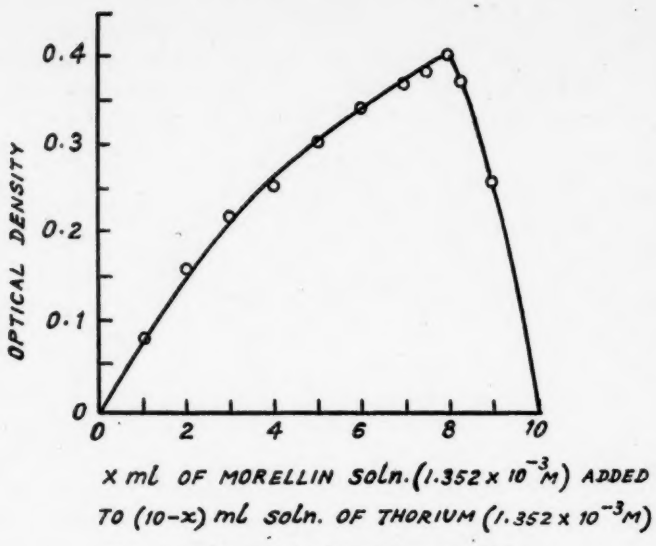
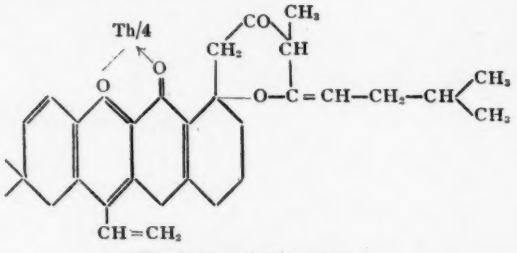


FIG. 4. Job's method of continuous variations.

the complex is, therefore, ThM_4, where M represents a molecule of morellin. The complex could, therefore, be represented as 8-co-ordinate thorium inner complex with the following formula:



Thorium-morellin complex.

The composition of the complex was verified by the slope ratio method of Harvey and Manning.[18] It was found that the ratio of the two reacting components in the complex was 3·96, thus agreeing with the structure given above.

SUMMARY

The spectrophotometric estimation of thorium has been studied by employing morellin which forms an orange-red complex in alcoholic medium. The complex is found to obey Beer's law at 515 mμ in the range 1·4 to

25 p.p.m. of thorium. It has been found that the complex is stable between the pH 5 and 7. Morellin to thorium mole ratio in the 8 co-ordinate inner complex of thorium is 4 : 1. Limits of tolerance of interfering ions during the estimation of thorium have also been ascertained.

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ASSIGNMENT OF THE RAMAN FREQUENCIES OF METHYL AND ETHYL BENZOATES AND ETHYL CINNAMATE

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1. Introduction

The Raman spectra of methyl and ethyl benzoates have been studied by several investigators—(1) Ghosh and Kar (1931), (2) Matsuo and Han (1933), (3) Kohlrausch and Pongratz (1933), (4) Murty and Seshadri (1939), (5) Herz *et al.* (1943) and (6) Hariharan (1954). The spectrum of ethyl cinnamate has been investigated by Harrand (1953) besides the earlier workers. Matsuo and Han have assigned the different frequencies observed in a series of alkyl esters of benzoic acid. Hariharan differs in his assignments of frequencies of methyl and ethyl benzoates from those of Matsuo and Han. In his studies of hydrogen bond formation in the mixtures of esters with phenol or methyl alcohol, the author has proposed to assign the various frequencies of esters. The assignments proposed by the author do not agree substantially with those of either Matsuo and Han or Hariharan.

2. Experimental

The experimental technique adopted has been described in the earlier communications by the author (1953).

3. Results

The Raman frequencies as recorded by the author are given below.

Table I

(i) *Methyl Benzoate*

138 (0), 170 (0), 217 (5), 359 (6), 535 (1), 619 (6), 676 (2), 812 (1 *b*), 825 (7), 968 ($\frac{1}{2}$), 988 ($\frac{1}{2}$), 1004 (10), 1027 (3), 1114 (2), 1161 (2), 1181 (2), 1280 (8 *b*), 1323 (1 *b*), 1450 (2 *b*), 1500 (2), 1603 (10), 1724 (7), 3067 (1 *b*).

(ii) *Ethyl Benzoate*

192 (7), 331 (5), 384 ($\frac{1}{2}$), 617 (7), 670 (4), 785 (2), 810 (2), 850 (7), 985 (5), 1002 (10), 1026 (2), 1109 (3), 1160 (3), 1278 (9), 1314 (2), 1367 (2),

TABLE I—(*Continued*)

1397 (2), 1454 (5), 1498 (2), 1603 (10), 1719 (8), 2934 (½), 2978 (½), 3066 (1).

(iii) *Ethyl Cinnamate*

178 (1 *b*), 273 (1 *b*), 341 (½), 408 (2), 458 (0), 580 (1), 594 (1), 622 (4), 722 (2), 740 (1), 774 (2), 843 (3), 871 (3 *b*), 928 (½), 991 (2), 1005 (7), 1029 (2), 1169 (3), 1184 (5), 1205 (5), 1270 (3 *b*), 1307 (3), 1335 (2), 1369 (2), 1395 (1), 1453 (4), 1498 (4), 1541 (3), 1577 (4), 1601 (8), 1639 (9), 1711 (5), 2829 (½), 2938 (½).

Three lines at 535, 988 and 1500 cm,$^{-1}$ in methyl benzoate 985 cm.$^{-1}$ in ethyl benzoate and six lines at 178, 341, 458, 740, 774 and 2829 cm.$^{-1}$ in ethyl cinnamate have been recorded for the first time by the author.

4. ASSIGNMENT OF THE LINES

The shifts at 615, 1001, 1025, 1158, 1177, 1595 and 3070 cm.$^{-1}$ are identified as the well-known frequencies of the phenyl group, because of the approximate constancy of the characteristic frequencies of the phenyl group shown by Murray and Cleveland (1941). Therefore the lines at 619, 1004, 1027, 1161, 1181, 1603 and 3067 cm.$^{-1}$ in methyl benzoate and 617, 1002, 1026, 1160, 1172, 1603 and 3066 cm.$^{-1}$ in ethyl benzoate can be identified as the frequencies arising out of the vibrations of the ring. The frequencies due to the C—H valence and deformation oscillations of the aliphatic group, 1450, 1500 cm.$^{-1}$ in methyl benzoate and 2934, 2978, 1367, 1454 and 1498 cm.$^{-1}$ in ethyl benzoate.

The low frequency lines at 138, 170, 217, 359 and 535 cm.$^{-1}$ in methyl benzoate and 192 (7), 331 (5) and 384 in ethyl benzoate can be attributed to the intermolecular oscillations.

There appears to be some uncertainty about the assignment of the frequencies of the group $\overset{\overset{O}{\|}}{C}—OR$. Matsuo and Han attribute the lines 1720, 1270 and 670 cm.$^{-1}$ as the characteristic vibrations of the above group, but Herz *et al.* have assigned 1720, 1120, 966 and 828 cm.$^{-1}$ to the inner vibrations of $CO.OCH_3$ group. Paranjpe and Savnur (1933) attribute the lines 1730, 1030 and 630 cm.$^{-1}$ as characteristic of the same group. Hariharan assigns 1720, 1110 and 670 cm.$^{-1}$ as the frequencies of the group $\overset{\overset{O}{\|}}{\underset{|}{C}}=O$. Except

Matsuo and Han none of the earlier workers assign the intense line at 1270 cm.$^{-1}$ as one of the frequencies of the group $\begin{matrix} O \\ | \\ C{=}O, \\ | \end{matrix}$ although this line occurs in all the benzoates. Hariharan suggests this line to arise out of some deformation oscillations involving the hydrogen atoms in the attached aliphatic group.

In an earlier communication (1953) the author, in identifying the frequencies of benzaldehyde, has assigned 1197, $\left.\begin{matrix} 1448 \\ 1493 \end{matrix}\right\}$, 1694 cm.$^{-1}$ to the group $\begin{matrix} C{-}C{-}H. \\ \| \\ O \end{matrix}$ In this assignment it is obvious that 1694 cm.$^{-1}$ is due to C=O and $\left.\begin{matrix} 1448 \\ 1493 \end{matrix}\right\}$ are due to C—H^{11} and C—H$^{\perp}$. Therefore 1197 cm.$^{-1}$ can be associated with C—C linkage between the ring carbon on the one hand and the aliphatic carbon on the other. Similarly the lines at 1181 cm.$^{-1}$ in methyl benzoate and 1172 cm.$^{-1}$ in ethyl benzoate, can be assigned to C—C link formed by the ring carbon and the aliphatic carbon of the group $\begin{matrix} O \\ \| \\ C{-}OCH_3. \\ | \end{matrix}$

It is difficult to assign either of the lines 619 and 676 cm.$^{-1}$ to the group $\begin{matrix} O \\ \| \\ C{-}OCH_3 \\ | \end{matrix}$ because these frequencies with comparable intensities are found in the spectrum of benzene.

Regarding the line at 1280 cm.$^{-1}$ in methyl benzoate and 1279 cm.$^{-1}$ in ethyl benzoate, Hariharan does not agree with the assignment made by Matsuo and Han as to their being one of the group frequencies of the group $\begin{matrix} O \\ \| \\ C{-}OR. \\ | \end{matrix}$

TABLE II

Some Frequencies of Benzene and Substituted Compounds

Benzene		1178	1584 1600

TABLE II—(*Continued*)

Benzaldehyde	..	1159	1197		1448 1493	1591	1694
Methoxy Benzene	..		1177	1244	1452	1587 1603	
Methyl Benzoate			1181	1280	1450	1603	1724

Some of the relevant frequencies of benzene and some of the substituted compounds are given in Table II. When the aldehydic group $\overset{O}{\overset{\|}{C}}—H$ is substituted in one of the hydrogens of benzene, some new frequencies, 1197, $\left.\begin{matrix}1448\\1493\end{matrix}\right\}$, 1694 cm.$^{-1}$ are recorded which can reasonably be assigned to the new group that has entered the compound by way of substitution. Similarly by the substitution of the methoxy group in place of one of the hydrogens, an intense line at 1244 cm.$^{-1}$ is recorded, which was not recorded either in benzene or benzaldehyde. This line can therefore be assigned to the vibrations of C—O bond which exists in methoxy benzene only.

Therefore 1280 cm.$^{-1}$ in methyl benzoate and 1278 cm.$^{-1}$ in ethyl benzoate can be ascribed to the vibrations of the C—O link in the group $\overset{O}{\overset{\|}{\underset{|}{C}}}—OR$.

Thus the lines at 1181, 1280 and 1724 cm.$^{-1}$ in methyl benzoate and 1172, 1278 and 1719 cm.$^{-1}$ in ethyl benzoate can be assigned to the frequencies of the group $\overset{O}{\overset{\|}{\underset{|}{C}}}—OR$ where R is either CH_3 or C_2H_5.

Similar assignments can be made in the case of ethyl cinnamate. The

group $-C=\overset{|}{C}-$ gets linked to the phenyl group through one of the carbons. Therefore 1205 cm.$^{-1}$ in ethyl cinnamate can be assigned to the C—C link formed by the C of the ring and C of the vinyl group and 1639 cm.$^{-1}$ can be ascribed to the vibrations of the C=C. A line at 1270 cm.$^{-1}$ is due to the vibrations C—O in the aliphatic side-chain. The assignment of the other frequencies are well known.

SUMMARY

The Raman spectra of methyl and ethyl benzoates, and ethyl cinnamates have been recorded in the liquid state at 42° C. Some new lines are reported. The lines at 1181, 1280 and 1724 cm.$^{-1}$ in methyl benzoate, and 1172, 1278 and 1719 cm.$^{-1}$ in ethyl benzoate are assigned to the group $\overset{O}{\overset{\|}{C}}-OR$ and 1205, 1270 and 1639 cm.$^{-1}$ are assigned to the group $-C=C$ in ethyl cinnamate.

The author expresses his sincere thanks to Professor S. Bhagavantam for his inspiring guidance.

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SOUND ABSORPTION COEFFICIENTS BASED ON INTENSITY MEASUREMENTS OF DIFFRACTION ORDERS

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1. Introduction

Biquard (1933) was the first to use the phenomenon of optical diffraction by an ultrasonic beam for the determination of ultrasonic absorption coefficients in liquids. This principle has been used by several workers (1934 and 1935) subsequently. More recent workers such as Willis (1947), Burton (1948) and Sette (1950) have used refined techniques and obtained very accurate results even at low frequencies of the order of 4 Mc/s. The above workers have made observations on the first order of diffraction. In the present investigation, however, the zero (or central) order was used for making measurements, as its intensity will be much higher than that of the first order. This makes the measurement more convenient without in any way affecting its accuracy. A wide frequency range from 7 to 50 Mc/s. was covered in these measurements.

2. Method of Measurement

When an ultrasonic beam passes through a liquid, the intensity of the beam decreases exponentially according to the relation $S_x = S_o e^{-2\alpha x}$. Biquard established that ultrasonic sound intensity is linearly proportional to the diffracted light intensity for small values of the former. The above relation can therefore be written in terms of the diffracted light intensities as $I_x = I_o e^{-2\alpha x}$, where I_x and I_o represent the intensity of the zero order at a distance x and at the origin of the source of sound respectively. It follows that

$$\log_{10} \frac{I_x}{I_o} = \text{constant} - 2\,\alpha x \log_{10} e.$$

The intensities of the zero order are measured by employing a 931-A photomultiplier tube as reported in an earlier communication (1955). The deflections θ_x and θ_o of the galvanometer connected to the photo-tube are proportional to the intensity I_x and I_o respectively so that the above relation can be written as

$$\log_{10}\frac{\theta_x}{\theta_o} = \text{constant} - 2ax\log_{10}e.$$

The experimental values of $\log_{10}\theta_x/\theta_o$ plotted against the distances x, give a straight line whose gradient gives the required value of 'a'. These values of 'a' so obtained are expressed in the standard form $a'/f^2 \times 10^{14}$ decibles sec.^{2}/metre.

The optical arrangement used in this investigation is extremely simple and shown in Fig. 1 which is self-explanatory. An intense parallel beam

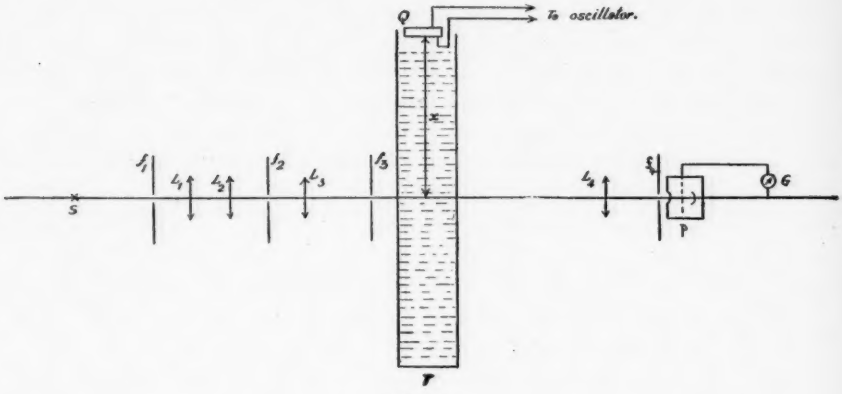

FIG. 1

of monochramatic light from a sodium source S is allowed to traverse the liquid contained in a cell T of dimensions $2 \times 2 \times 12$ inches. A diaphragm f_3 is used before the cell to ensure that the light traverses a small region of the sound waves. The bottom of the cell contains a glass plate inclined at 45° to the horizontal to prevent formation of standing waves. A number of x-cut quartz crystals with 1-inch square radiating surface are used at their fundamentals and odd harmonics to cover the frequency range from 7 to 50 Mc/s. The liquids used in this investigation are thoroughly distilled and pure. The crystal holder is mounted so that it is movable by regular steps in a direction normal to the axis of the optical system, without any tilt, in order to avoid a change in the diffraction of light by a change in the angle of incidence. It is important to note that the intensity of the diffracted light is only proportional to the sound intensity for small values of the latter, since at higher intensities, multiple diffraction takes place, causing the light to be diffracted back from the diffraction spectra into the central image. Hence, to avoid the multiple diffraction effects, the sound intensity is made small enough by always working the oscillators at low power to excite only the first

TABLE I

Liquid	Eiquard $f = 8$ Mc/s.	Pellam and Galt $f = 15$ Mc/s.	Rapuano $f = 75$–280 Mc/s.	Author $f = 7{\cdot}02$ Mc/s.	Author $f = 21{\cdot}10$ Mc/s.	Author $f = 48{\cdot}73$ Mc/s.
1. Benzene ..	796 (17° C.)	690·0 (21·8° C.)	780·0 (25° C.)	743·7	..	..
2. Carbon tetrachloride	..	464·0 (23·5° C.)	490·0 (24° C.)	462·8	..	..
3. Petroleum ether ..	76·0 (20° C.)	..	..	88·7	85·6	..
4. Toluene ..	72·5 (19° C.)	..	..	84·7	88·2	..
5. Acetone ..	23·3 (21° C.)	..	..	33·5	..	34·0
6. Ethyl acetate ..	..	62·0 (24·3° C.)	..	62·1	65·2	..
7. Methyl acetate ..	..	62·0 (19·0° C.)	..	66·0	64·4	..
8. Amyl acetate ..	..	64·0 (29·2° C.)	..	62	62·3	..
9. Methyl alcohol ..	..	32·0 (19·3° C.)	27·1 (21° C.)	33·8	34·1	26·5
10. Meta xylol ..	64·8 (19° C.)	..	..	66·1	64·4	..
11. Ethyl alcohol ..	..	20·0 (2° C.)	46·7 (22° C.)	..	..	35·3

orders of diffraction suppressing second and higher orders. The crystal holder is adjusted before commencing the measurements such that the two diffraction orders are equally intense on either side of the zero order. This ensures that the light beam is normal to the ultrasonic beam. Intensity measurements using the photo-tube are then made over a length of 12 cm. of the liquid column at three frequencies 7·02 Mc/s. 21·1 Mc/s., and 48·73 Mc/s. for different liquids.

However, this technique of employing optical diffraction for the determination of absorption coefficients could not be extended beyond 50 Mc/s., because of the difficulty in exciting intense diffraction orders at higher frequencies in the normal position of the ultrasonic grating. At 50 Mc/s., it is found that the sound wave gets completely absorbed making it impossible to make intensity measurements beyond 2 cm. of the liquid column.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The values of absorption coefficients obtained for different liquids by this method are given in Table I. The temperature of observation is maintained constant at 28·5° C. within an accuracy of $\pm 0{\cdot}5°$ C. The values of absorption coefficients obtained by other workers are given for comparison, showing the temperature of observation in brackets. The values obtained by this method are accurate a little better than 10 per cent.

It can be seen from Table I that the values of absorption coefficients compare well with the values of other workers. It is found that at the three frequencies studied, $\alpha'/f^2 \times 10^{14}$ remains constant within limits of experimental error. Biquard's value for benzene is higher than the value obtained and is also higher than Pellam and Galt's or Rapuano's. The value obtained by this method agrees fairly well with that of Rapuano, when allowance is made for the temperature. In other liquids, the agreement is fairly satisfactory when temperature changes are taken into account.

4. SUMMARY

Sound absorption coefficients for a large number of liquids are determined by using a 931-A photo-multiplier tube. Observations are made on the zero order diffraction spectrum, the change in intensity of this spectrum being an index of the sound absorption in liquid. The method gives satisfactory results over a wide frequency range from 7 to 50 Mc/s. covered in this investigation and the values obtained compare well with those of other workers in the literature.

In conclusion, I wish to express my deep indebtedness to Professor S. Bhagavantam for the invaluable suggestions and the keen interest he took during the entire progress of this work.

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POTENTIAL ANTITUBERCULAR COMPOUNDS

Part III. 7-Aminoflavone*

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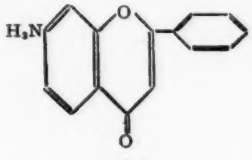
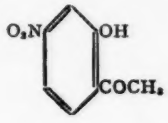
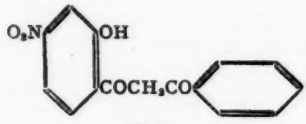
Extracts of *Primula malacoides* have been found to exhibit antibacterial activity against *Mycobacterium tuberculosis* and other gram-positive and gram-negative bacteria.[1] The antibacterial substance was subsequently identified as flavone, which inhibited the growth of *M. tuberculosis* at a concentration of 0·05 mg. per ml.[2] Toxicity tests showed that 0·25 per cent. of flavone in a mouse diet was acceptable and did not interfere with weight increase; the highest tolerated subcutaneous dose of flavone in corn oil was 400 mg. per kg. of body weight. It seemed desirable therefore to synthesize 7-amino-flavone (I), which may be regarded as a derivative of 4-aminosalicylic acid (PAS). Aminoflavones are of interest from another point of view. In a report on the extraction of "bioflavonoids" from the thymus gland[3] Szent-Györgyi has suggested that the animal body attaches an amino group to the flavone molecule to make it "fit into its machinery".



(I)



(II)

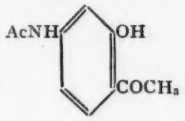


(III)

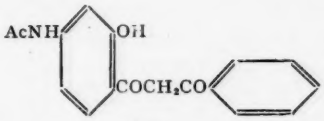
Two methods have proved to be suitable for the synthesis of 7-amino-flavone. The starting material for one route was 2-hydroxy-4-nitroaceto-phenone (II), which was prepared by Paranjape[4] and will be described in a later paper. By heating the ketone (II) with benzoyl chloride and anhydrous

* Parts I and II: *Proc. Indian Acad. Sci.*, 1949, **29 A**, 196; 1950, **32 A**, 357.

potassium carbonate in acetone for 4 hours, *O*-benzoylation and transformation to the diketone (III) were effected in one operation. The *O*-benzoyl derivative, however, was isolable if the reaction time was reduced to an hour. Cyclization of (III) with concentrated sulphuric acid yielded 7-nitroflavone, which was then reduced to 7-aminoflavone (I) by means of zinc dust and acetic acid. 7-Aminoflavone was also prepared from 4-acetamido-2-hydroxyacetophenone (IV).[5] Conversion of (IV) to the diketone (V) was possible by either of two methods: (*a*) treatment of the *O*-benzoyl derivative (conveniently prepared by means of benzoyl chloride and potassium carbonate in acetone) with caustic potash in pyridine according to Wheeler,[6] or (*b*) prolonged treatment of the ketone (IV) with benzoyl chloride and potassium carbonate in boiling acetone. Cyclization of the diketone (V) with sulphuric acid at 0° gave 7-acetamidoflavone which was then de-acetylated to 7-aminoflavone (I) by hot 10% hydrochloric acid.

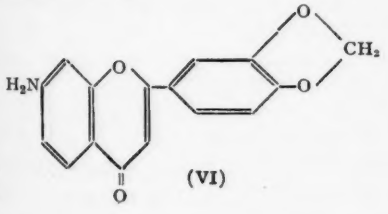


(IV)

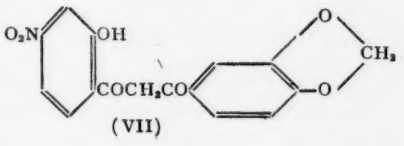


(V)

The methylenedioxy group occurs in many natural products which are physiologically active. Piperonal and its azomethine with *p*-aminobenzoic acid have high antifungal activity and low toxicity.[7] Piperonylic acid is active against *M. tuberculosis* at a dilution of 0·05 mg./ml.[8] Sesamin, which is a constituent of the unsaponifiable fraction of sesame oil and contains two methylenedioxyphenyl groups, has been reported[9] to inhibit the growth of *M. tuberculosis* at a dilution of 1 in 50,000. The influence of a methylenedioxy group on antitubercular activity was therefore studied by the preparation of 7-amino-3′: 4′-methylenedioxyflavone (VI). 2-Hydroxy-4-nitroacetophenone was converted to the diketone (VII) by prolonged treatment with piperonylyl chloride and potassium carbonate; cyclization and reduction then led to (VI).



(VI)



(VII)

Antibacterial tests on the compounds synthesized in the present work have been carried out by Mr. M. L. Khorana and Mrs. S. R. Shah, and they will be discussed elsewhere. Against *M. tuberculosis* (B.C.G. strain) 7-aminoflavone (I) and flavone had about the same activity, the minimum growth-inhibiting concentration being 50γ/ml.; but 7-aminoflavone inhibited the growth of *B. typhosus* at a concentration of 20γ/ml., while the necessary concentration of flavone was 40γ/ml. Both flavone and 7-aminoflavone inhibited the growth of *Staph. aureus* at a concentration of 80γ/ml. Dr. V. C. Barry, Director of Laboratories, Medical Research Council of Ireland, to whom we are greatly indebted, has reported that 7-aminoflavone completely inhibited *M. tuberculosis* H37Rv in Proskauer and Beck synthetic medium at a dilution of 50,000, allowing full growth at 75,000. When 5% serum was incorporated in the medium there was a partial inhibition of growth at 10,000 and full growth at 150,000. In mice it did not appear to show any anti-tubercular activity.

EXPERIMENTAL

2-*Hydroxy*-4-*nitroacetophenone* (*II*), crystallizing in yellow needles, m.p. 66°, was prepared as described by Paranjape.[4]

2-*Benzoyloxy*-4-*nitroacetophenone*.—2-Hydroxy-4-nitroacetophenone (0·2 g.), acetone (20 c.c.), benzoyl chloride (0·3 c.c.) and potassium carbonate (0·8 g.) were refluxed for one hour. Acetone was removed by distillation, and the addition of water gave an oily product, which soon solidified. It crystallized from ethanol in pale yellow, stout prisms and rods, m.p. 105–06° (Found: C, 63·6; H, 3·9. $C_{15}H_{11}O_5N$ requires C, 63·1; H, 3·9%).

2-*Hydroxy*-4-*nitrodibenzoylmethane* (*III*).—2-Hydroxy-4-nitroacetophenone (2 g.), acetone (60 c.c.), benzoyl chloride (3 c.c.) and anhydrous potassium carbonate (10 g.) were refluxed for 4 hours. The colour of the solution gradually deepened and a bulky orange-red precipitate was formed. Acetone was removed by distillation, the orange residue was taken up in water (150 c.c.) and acidified with hydrochloric acid. The bright yellow diketone was collected, dried (2·5 g.), and crystallized from benzene. The deep yellow needles melted at 196° (Found: C, 63·7; H, 4·0; N, 4·8. $C_{15}H_{11}O_5N$ requires C, 63·1; H, 3·9; N, 4·9%). The substance gives a deep cherry-red colour with ferric chloride.

7-*Nitroflavone*.—2-Hydroxy-4-nitrodibenzoylmethane (III; 1 g.) was dissolved in cold concentrated sulphuric acid (10 c.c.) and left overnight. The solution was then poured into crushed ice. The bulky white precipitate (0·8 g.) crystallized from 50% acetic acid in cream coloured, shining needles,

m.p. 233–34° (Found: C, 67·4; H, 3·1; N, 5·5. $C_{15}H_9O_4N$ requires C, 67·4; H, 3·3; N, 5·2%).

7-Aminoflavone (*I*).—7-Nitroflavone (0·2 g.) and zinc dust (0·8 g.) in boiling alcohol (50 c.c.) were treated with glacial acetic acid (2 c.c.) added in 4 lots at intervals of 10 minutes. The zinc dust was filtered off, the filtrate concentrated to 10 c.c., cooled, diluted with water (50 c.c.), and allowed to stand overnight. The crystalline product was crystallized from 50% alcohol, and the yellow needles melted at 186° (Found: C, 75·6; H, 4·9; N, 6·0. $C_{15}H_{11}O_2N$ requires C, 75·9; H, 4·7; N, 5·9%).

4-Acetamido-2-hydroxyacetophenone (IV), colourless needles, m.p. 142°, was prepared by the method of Julia.[5]

4-Acetamido-2-benzoyloxyacetophenone.—4-Acetamido-2-hydroxyacetophenone (1 g.), acetone (30 c.c.), benzoyl chloride (1·2 c.c.) and anhydrous potassium carbonate (4 g.) were refluxed for 3 hours. The acetone was removed by distillation and water was added. The oily product soon solidified and crystallized from methanol in white prisms (1·1 g.), m.p. 125° (Found: C, 68·2; H, 5·3; N, 4·4. $C_{19}H_{15}O_4N$ requires C, 68·6; H, 5·1; N, 4·7%).

4-Acetamido-2-hydroxydibenzoylmethane: *Method* (*A*).—4-Acetamido-2-benzoyloxyacetophenone (0·4 g.) was dissolved in pyridine (3 ml.) and warmed to 50°. Pulverised potassium hydroxide (0·2 g.) was added and the mixture was stirred for 15 minutes at 50°. A bulky yellow precipitate of the potassium salt of the diketone was formed. On acidification with 10% acetic acid the diketone (270 mg.) was crystallized from alcohol. The yellow leaflets had m.p. 165° (Found: C, 68·6; H, 5·0; N, 4·4. $C_{17}H_{15}O_4N$ requires C, 68·7; H, 5·1; N, 4·7%). The substance gives a cherry-red colour with ferric chloride.

Method (*B*).—4-Acetamido-2-hydroxyacetophenone (5 g.), benzoyl chloride (4 ml.), acetone (150 ml.), and anhydrous potassium carbonate (20 g.) were refluxed for 7 hours. The mixture became deep yellow in colour. Worked up as usual, the yellow product (5·5 g.) crystallized from alcohol in yellow leaflets, m.p. and mixed m.p. with the product from method (A), 165°.

7-Acetamidoflavone.—4-Acetamido-2-hydroxydibenzoylmethane (1 g.) in cold concentrated sulphuric acid (15 ml.) was allowed to stand for two hours. The product obtained by the addition of ice crystallized from alcohol in white needles (0·7 g.), m.p. 272° (Found: C, 72·9; H, 4·7; N, 4·7. $C_{17}H_{13}O_3N$ requires C, 73·1; H, 4·7; N, 5·0%). The substance gives a blue fluorescence in concentrated sulphuric acid.

7-Aminoflavone (I).—7-Acetamidoflavone (0·5 g.) was boiled for 30 min. with 10% hydrochloric acid (25 ml.). The solution was cooled, and the acid neutralized by sodium bicarbonate. The yellow precipitate (320 mg.) crystallized from 50% alcohol in yellow needles, m.p. 186°, not depressed by mixing with 7-aminoflavone obtained by the reduction of 7-nitroflavone.

2-Hydroxy-4-nitro-3′: 4′-methylenedioxydibenzoylmethane (VII).—2-Hydroxy-4-nitroacetophenone (1 g.), acetone (30 c.c.), piperonylyl chloride (from 1·5 g. of piperonylic acid) and potassium carbonate (4 g.) were refluxed for 5 hours. The orange-red potassium salt of the diketone obtained after removing acetone was acidified with acetic acid. The diketone (1·2 g.) crystallized from benzene in orange-yellow plates and needles, m.p. 237° (Found: C, 57·9; H, 3·1. $C_{16}H_{11}O_7N$ requires C, 58·3; H, 3·3%).

7-Nitro-3′: 4′-methylenedioxyflavone.—The diketone (VII; 0·8 g.) was dissolved in concentrated sulphuric acid (10 c.c.) and allowed to stand overnight. After pouring in crushed ice a dirty yellow product separated (0·5 g.). It crystallized from chlorobenzene in yellow leaflets, m.p. 287° (Found: C, 62·1; H, 2·9; N, 4·6. $C_{16}H_9O_6N$ requires C, 61·7; H, 2·9; N, 4·5%).

7-Amino-3′: 4′-methylenedioxyflavone (VI).—7-Nitro-3′: 4′-methylenedioxyflavone (0·25 g.), zinc dust (0·5 g.) and alcohol (50 c.c.) were refluxed, and acetic acid (4 c.c.) was added during 30 minutes. The alcoholic solution was filtered and concentrated. 7-Amino-3′: 4′-methylenedioxyflavone, which separated as light yellow needles, was recrystallized from alcohol, and had m.p. 278° (Found: C, 68·5; H, 4·0; N, 4·9. $C_{16}H_{11}O_4N$ requires C, 68·3; H, 3·9; N, 4·9%).

SUMMARY

7-Aminoflavone has been synthesized in view of its relationship to 4-aminosalicylic acid (PAS) and the reported antitubercular activity of flavone.

By heating 2-hydroxy-4-nitroacetophenone with benzoyl chloride and potassium carbonate in acetone *O*-benzoylation and the Baker-Venkataraman transformation were both effected in one operation. Cyclization of the diketone and reduction gave 7-aminoflavone, which was also prepared from 4-acetamido-2-hydroxyacetophenone by conversion to the corresponding dibenzoylmethane, cyclization and hydrolysis of the *N*-acetyl group. 7-Amino-3′: 4′-methylenedioxyflavone was synthesized similarly for antitubercular tests, since piperonylic acid has considerable activity.

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